ABSTRACT

SEIFIKAR, SAFOURA. Texture and Magnetocrystalline Anisotropy in NiFe$_2$O$_4$ Thin Films Deposited via Chemical Solution Deposition. (Under the direction of Justin Schwartz).

Spinel nickel ferrite with the chemical formula Fe$^{3+}$[Ni$^{2+}$Fe$^{3+}$]O$_4$ (NFO) has attracted highly attentions for many applications due to its room temperature magnetic behavior, moderate electrical resistivity and, high Curie temperature. Along with other magnetic spinel cubic ferrites including CoFe$_2$O$_4$ and MnFe$_2$O$_4$, NFO has long been considered as the magnetostrictive phase to fabricate magnetoelectric (ME) composites. One of the approaches to improve the ME response of the composites is to enhance the magnetostriction of the magnetic phase by texturing along its magnetic easy axis direction.

In this work, spinel cubic NiFe$_2$O$_4$ (NFO) thin films are derived via chemical solution deposition (CSD) technique. The films grown on Si substrates show a granular microstructure and surface roughness of 3 nm. The effects of varying the processing condition including pyrolysis and annealing temperature have been studied on the microstructure and the resulting magnetic properties. Microstructural studies confirm the formation of randomly oriented, phase-pure spinel nickel ferrite on Si substrates. It is shown that the pyrolysis temperature does not affect the microstructure and resulting magnetic properties, while increased the grain size as a results of increased annealing temperature influences the magnetic properties.

Magnetoelectric thin film multilayers are prepared also using NFO as the magnetostrictive phase and PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT) as the piezoelectric phase via CSD. The PZT/NFO composite microstructures are investigated through TEM and SEM studies and the interface is engineered to minimize the elemental interdiffusion between phases and the substrate. The
dielectric property of the piezoelectric phase and the magnetic response of the magnetic phase are investigated. The addition of a Pt intermediate layer resulted in an improved dielectric properties obtained in Si/NFO/Pt/PZT composite configuration.

To improve the magnetostriction response of the NFO layer, same CSD method is employed to grow highly textured NFO thin films on Si/SiO$_2$/TiO$_x$/Pt and Al$_2$O$_3$ (0001) substrates. The deposited NFO thin films on Si/SiO$_2$/TiO$_x$/Pt substrates show complete uniaxial out-of-plane texture in the <111> direction with random in-plane orientation. While X-ray $\varphi$-scanning indicates the <111> out-of-plane texture as well as <110> in-plane epitaxial relationships in two crystallographic variants between the films and the Al$_2$O$_3$ (0001) substrates. As the NFO magnetic easy-axis is <111>, the out-of-plane magnetization for both textured thin films exhibits improved $M_r/M_s$ (remanent) ratios with respect to the randomly oriented NFO films on Si substrates. However, compared to the uniaxially textured NFO films on platinized silicon, the films on the Al$_2$O$_3$ (0001) substrates show 10% increase in out-of-plane remanent ratio and 20% reduction in coercivity. In addition, both textured NFO thin films show enhanced magnetostrictive response compared to the randomly oriented films on the Si substrates. The improved out-of-plane magnetic anisotropy in the textured films is comparable to epitaxial NFO films of similar thickness deposited by pulsed laser deposition and sputtering. Microstructural studies show that texturing initiates by nucleation of (111) planes at the film/substrate interface and decreases as the film thickness decreases.
Texture and Magnetocrystalline Anisotropy in NiFe$_2$O$_4$ Thin films Deposited via Chemical Solution Deposition

by
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DEDICATIONS

To my beloved, friend and husband, Mostafa, whom I owe my love and trust and whom I always share my reverie. This would have never happened without his unsparing supports.

And,

To my parents, Ahmad and Azra, who taught me the value of patience.
BIOGRAPHY

Safoura Seifikar was born in Hamedan, Iran on September 12nd, 1978 to Ahmad and Azra. After finishing her high school in NODET (National Organization for Development of Exceptional talents), she got admitted to Sharif University of Technology (Tehran, Iran) in 1996 majoring in Materials Science and Engineering. In 2000, she got admitted to the School of Materials Science at Sharif University of Technology. After taking the Master’s degree, Safoura started her job in Iranian Fuel Conservation Organization as an engineer and a project manager in the fields of renewable energies. She came to US in Aug., 2009 and joined Prof. Schwartz group at North Carolina State University and took his PhD in Materials Science and Engineering in March 2013.
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(d, h) 60 nm thicknesses

Figure 7-8 TEM cross-sectional image of the 60 nm Al$_2$O$_3$-NFO film

Figure 7-9 Room temperature in-plane and out-of-plane magnetization hysteresis for the 60 nm-thick biaxially textured Al$_2$O$_3$-NFO films

Figure 7-10 Room temperature out-of-plane coercivity and $M_r/M_s$ ratio for the Al$_2$O$_3$-NFO films as a function of thickness. Values for the 110 nm-thick randomly oriented Si-NFO and the uniaxially textured Pt-NFO films are shown for comparison.

Figure 7-11 X-ray diffraction patterns of the textured NFO films deposited onto the (0001) sapphire substrates. The films are pyrolyzed at temperatures ranging from 100°C to 500 °C and annealed at 750 °C for 10 min. The inset shows the changes of (111) Lotgering factor (f) as a function of pyrolysis temperature.

Figure 7-12 Top-view HIM micrographs of single-layer NFO films on (0001) sapphire substrates, pyrolyzed at (a,b) 100 °C and (c,d) 500 °C for one minutes.

Figure 7-13 X-ray diffraction patterns of the textured NFO films deposited on the (0001) sapphire substrates, pyrolyzed at 400 °C for 1 min and annealed at temperatures ranging from 700°C to 1000 °C.

Figure 7-14 Top-view HIM micrographs and corresponding AFM images of single-layer NFO films on (0001) sapphire substrates and annealed at (a,c) 750 °C and (b,d) 1000 °C for 10 minutes.

Figure 7-15 X-ray diffraction patterns of textured NFO films deposited on the (0001) sapphire substrate, using 0.2 M and 0.5 M solutions. The inset shows the X-ray φ-scan of the (01-12) Al$_2$O$_3$ and (440) NFO in the epitaxial films deposited using 0.2M solution.

Figure 7-16 (a,b)Top-view HIM micrographs of the epitaxial (111) NFO thin films deposited on the (0001) sapphire substrates. (c) schematic of two rotated (111) NFO planes in two variants with 60 or 180 degree rotation.

Figure 7-17 (a) Selected area electron diffraction (SAED) pattern of the (111) NFO
and (0001)sapphire and (b) its indexed pattern................................. 176
CHAPTER 1
INTRODUCTION AND OVERVIEW

1.1 Research Motivation

Spinel ferrites with the general chemical formula AFe$_2$O$_4$ (A is an divalent metallic cation such as Co$^{2+}$, Mg$^{2+}$ and Ni$^{2+}$) are of technical interest for their broad range of tunable physical properties$^1$. With moderate electrical resistivity, room temperature ferrimagnetic behavior, low magnetic loss, and relatively high Curie temperature (585 °C)$^2$, NiFe$_2$O$_4$ (NFO), is one of the most important spinel ferrites. These properties accompanied with its high thermal and chemical stability makes NFO particularly interesting for many technological applications such as high frequency microwave devices including circulators and phase shifters$^3$-$^5$, spintronics$^6$, and magnetic recording devices$^3$-$^5$,$^{12}$-$^{15}$. Also NFO as one of the magnetic ferrites with magnetostrictive response at room temperature, has shown efficient mechanical bonding to Pb[Zr$_x$Ti$_{1-x}$]O$_3$ (PZT), to fabricate magnetoelectric composites$^7$-$^{16}$.

In a magnetic material, magnetic anisotropy is defined as dependence of magnetic properties of the material on the direction in which it is measured. It can be intrinsic as a result of crystal structure (magnetcocrystalline anisotropy), and/or extrinsic due to shape effects (shape anisotropy). Depending on the application, stronger or weaker magnetic anisotropy in the material is desired. For instance, in transformers and magnetic inductors that require high susceptibility, minimizing the magnetic anisotropy is important$^{17}$,$^{18}$. Conversely, a higher
magnetic anisotropy allows greater thermal stability of magnetic bits, and hence can lead in a reduction of the bit size in memory devices \(^{19}\). Also, in multiferroic composites, having the magnetic phase textured along its easy axis direction, results in maximizing the magnetostrictive property and leads to enhanced magnetoelectric response of the composite. Although thin films are an advantageous geometry for device applications, few studies on textured NFO thin films have been reported, and the only limited studies on epitaxial or textured films involve films prepared by pulsed laser deposition\(^{6,20-22}\), DC sputtering\(^{23,24}\). In addition the effect of the crystallographic texture on the magnetic properties of the NFO thin films has not been thoroughly studied.

These processing techniques tend to be more complex and more expensive than chemical solution deposition (CSD) approaches. In addition to ease in processing and its low cost, CSD provides benefits in tailoring the films’ composition and structure.

In this work, in addition to develop a chemical route to deposit spinel cubic phase-pure NFO thin films on different substrates, growth of textured NFO thin films via CSD are discussed and the effect of the crystallographic texture on the magnetic behavior of the films is studied. The fabrication of multiferroic NFO/PZT laminated thin film composites via CSD and the microstructure and properties of the composites are reviewed.
1.2 Dissertation Structure

It is tried to design the structure of this dissertation to provide a straightforward narrative. Chapter 1 serves as an overall introduction and discusses the motivation for the research. Chapter 2 provides the reader with background information on magnetic materials, magnetic anisotropy, ferrites and magnetoelectric composites materials. Chapter 4 discusses on growth of randomly-oriented nickel ferrite thin films on Si substrates. Microstructural and magnetic studies have been performed on the grown films to optimize the deposition and annealing conditions. Chapter 5 reviews characterization and test results of the magnetoelectric NFO/Pb(Zr0.52Ti0.48)O3 laminated thin film composites fabricated via CSD. Chapter 6 discusses on growth, characterization and test results of uniaxially textured NFO thin films on Si/SiO2/TiOx/Pt substrates based on a published paper:


In Chapter 7, growth and characterization of textured NFO thin films on c-plane sapphire substrates with epitaxial relationships with the substrate is discussed based on the published paper:


In Chapter 6 and 7, effect of the crystallographic texture on the magnetic properties is investigated. Chapter 8 serves as a summary and presents the conclusions drawn from the data presented in Chapters 4 to 7 followed by suggested future work.
1.3 References


2.1 Magnetism

The response of a material to applying an external magnetic field $H$ is called magnetic induction or magnetic flux density $B$:

$$B = H + 4\pi M$$  \hspace{1cm} \text{eq. 2.1}

where $M$ is the magnetization intensity of the material. In an atom, magnetization is as a result of interactions between the external magnetic field and the magnetic field due to electron spin and orbital motion. The magnitude of the magnetization $M$ is defined as the total magnetic moment per unit volume $^1$

$$M = \frac{\mu N}{V}$$  \hspace{1cm} \text{eq. 2.2}

where $\mu$ is the magnetic moment, $N$ is the number of magnetic moments and $V$ is the volume of the material $^1$.

2.1.1 Magnetic Materials

Magnetic materials are classified based on their response to the magnetic field and their magnetic orders.
**Diamagnetic Materials**

By definition, diamagnetic materials have no intrinsic magnetic moment $^2,^3$. In diamagnetic materials, the spin and orbital moments of the atoms are oriented so that the atom has closed-shell electronic structure (monoatomic rare gas). The polyatomic gases (e.g. H$_2$ and N$_2$) are diamagnetic also due to their filled electron shells and no net magnetic moment per molecule. So are some ionic (e.g. NaCl) and most of the covalent solids (e.g. Si, Ge and diamond) with closed-shell electronic structures $^3$.

In a diamagnetic material, an external magnetic field (H) induces antiparallel magnetic dipoles with respect to the applied field $^1$. The M-H behavior of these materials shows a linear relationship with small negative slope (Figure 2-1).

**Paramagnetic Materials**

Paramagnetic materials are composed of atoms or ions with intrinsic magnetic dipoles because of non-cancelled spin and orbital components. Due to incomplete inner shells, such as those of the transition metal ions and rare earth ions, they can have a large net magnetic moment $^3$. The magnetic moments are oriented in the presence of an applied magnetic field but after removal of the magnetic field, thermal vibrations cause randomization (Figure 2-2) $^{1,2}$. The M-H behavior of paramagnetic materials exhibits a linear relationship with a positive slope (Figure 2-1).
Figure 2-1 M-H behavior of a diamagnetic and a paramagnetic material.

*Antiferromagnetic Materials*

Due to non-cancelled spin and orbital components, antiferromagnets have intrinsic magnetic dipoles. With an ordered arrangement of antiparallel aligned spins on different sublattices, these materials have no net spontaneous magnetization (Figure 2-2)\(^4\).
Figure 2-2 Magnetic dipole distributions in (a) paramagnetic, (b) ferromagnetic, (c) antiferromagnetic and (d) ferrimagnetic materials after removal of the magnetic field (H=0)

Ferromagnetic Materials

Ferromagnetism, which occurs in transition metals, results from unpaired electrons and is ruled by the electron spins. The contribution from orbital electron motion is negligible. In the demagnetized state, a ferromagnet does not have a net magnetization and it is divided into several small regions called “magnetic domains”. Each domain is formed from spins aligned parallel to each other. Each domain is magnetized spontaneously to the saturation value but the directions of magnetization of each domain are such that they cancel out each other and hence the whole specimen does not show a net magnetization (demagnetized state). Applied external magnetic field (H) causes some domains to grow and consume the other and the magnetization direction to rotate to the magnetic field direction (Figure 2-3).
The net magnetization of ferromagnetic materials changes from zero to a saturation value ($M_s$) by applying an external magnetic field; $M_s$ is the maximum magnetization in a ferromagnetic material. When the magnetic field is decreased from saturation point (in reversed direction), the magnetization of the ferromagnetic material does not retrace its original path of values and the material exhibits a magnetization hysteresis loop (Figure 2-3). The ferromagnetic materials are different widely in their magnetization behavior. If a small applied magnetic field causes saturation, the material is said to be magnetically soft. In contrast, when the saturation requires large applied magnetic field, the material is magnetically hard.

In a magnetization hysteresis loop, the coercive field ($H_c$) is defined as the magnetic field required to be applied in the opposite direction to reduce the magnetization of the magnetized
substance to zero (demagnetized state). The Remnance magnetization \((M_r)\), by definition, is the remaining magnetization in the material after the magnetic field is removed.

The shape of the M-H curve of the ferromagnetic materials (the \(H_c, M_r\) values) and the strength of the field at which the saturation magnetization is attained are grain structure-sensitive properties, whereas the magnitude of \(M_s\) is only depends on the material chemistry and crystal lattice structure. Depending on the application, material with large or small \(H_c\) and/or \(M_r\) is desired.

A ferromagnet exhibits paramagnetic behavior above its Curie temperature \((T_c)\). Increasing the temperature above \(T_c\) brings about a disturbance in the spin arrangement and results in completely random orientation of spins. At this temperature, the ferromagnet loses its spontaneous magnetization and becomes a paramagnet.

**Ferrimagnetic Materials**

Like ferromagnets, ferrimagnetic materials exhibit a spontaneous magnetization at room temperature. Ferrimagnetic materials also have magnetic domains and show hysteretic behavior that is similar to ferromagnetic materials (Figure 2-3). In ferrimagnetic materials, the spins of two cations located in two different sites are oppositely oriented. However, one of the magnetic spins is stronger than the other, hence the result is a non-zero, net spontaneous magnetization (Figure 2-2). Similar to ferromagnetic materials, ferrimagnetic materials become paramagnet at above a certain temperature (Curie, \(T_c\)). Furthermore, the above discussion on hysteresis and magnetization behavior of the ferromagnetic materials is
equally valid for ferromagnetic materials. Ferrite oxides, which will be discussed later in this section, are the most important ferrimagnetic substances.

2.1.2 Magnetization Measurement

Several methods are used to measure the magnetic behavior of materials. Among the measurement tools, vibrating-sample magnetometer (VSM) and superconducting quantum interference devices (SQUID) are most commonly used due to their high precision and sensitivity to measure the magnetization of the very small mass specimens and weak magnetic behavior.

**VSM**

VSM first invented by S. Foner (1959), measures the magnetization of a material based on the flux change in a coil when a magnetized sample in a DC magnetic field is oscillated at a low frequency. The small sample is attached to the end of a nonmagnetic rod and inserted into the VSM chamber. The schematic of a VSM is illustrated in Figure 2-4.
Moving the magnetic sample induces an AC field in the detection coils (pickup coils); the magnitude of the AC field is proportional to the magnetic moment of the sample. VSM is very sensitive, measuring magnetic moments as low as $10^{-5}$ emu and can be used for both weak and strong magnetic substances at high and low temperature $^3$.

**SQUID**

A superconducting quantum interference device (SQUID) is capable of measuring very small changes in magnetic field with higher sensitivity than VSM; as low as $10^{-7}$ emu. In a SQUID, two pieces of a superconducting material are separated by a very thin layer of an insulating material. The critical current density of the superconductor is changed by the presence of a
very small field. The SQUID uses this change in current to detect the small magnetic field \(^3\). This device works based on the tunneling of superconducting electrons across the insulating gap (Josephson junction); a schematic is shown in Figure 2-5.

![Figure 2-5 SQUID Flux sensor](image)

It acts as a very high-sensitivity fluxmeter, in which the integration is performed by counting voltage steps. It is of such high sensitivity that in a working instrument the magnetic field is held exactly constant by a superconducting shield, and the sample is moved slowly through a superconducting pickup coil coupled to the SQUID while flux quanta are counted. As the specimen is moved slowly through the ring, a changing magnetic flux through the ring generates a voltage and current in the ring, according to Faraday’s Law. The induced current adds to the measuring current in one junction, and subtracts in the other. In SQUID the direct experimental result is a plot of the sample magnetic moment vs the applied field \(H\).
2.1.3 Magnetic Anisotropy

Magnetic anisotropy is defined as dependence of magnetic properties of a material on the direction in which it is measured. It strongly affects the shape of the M-H curve, hysteresis loop in ferro/ferrimagnetic materials.

Depending on the application, stronger or weaker magnetic anisotropy in the material is desired. For instance, a higher magnetic anisotropy allows greater thermal stability of magnetic bits, and hence can lead in a reduction of the bit size in memory devices. Conversely, in transformers and magnetic inductors that require high susceptibility, minimizing the magnetic anisotropy is important. Therefore, understanding the mechanisms of the magnetic anisotropy, and the ability to manipulate it, are crucial to the technological use of ferro/ferrimagnetic materials.

Magnetic anisotropy can be intrinsic to the material crystal structure (magnetocrystalline anisotropy) or can be extrinsic (e.g. shape and, stress anisotropy).

Magnetocrystalline Anisotropy

Similar to other material characteristics, the magnetization vector in a crystal is not isotropic and the total energy of the magnetic crystal depends on the orientation of the magnetization vector with respect to the crystallographic direction. This phenomenon is known as magnetocrystalline anisotropy and results from spin-orbit interactions in the lattice structure. In a lattice structure, the easy axis direction is defined as the crystallographic direction in which the crystal energy is minimum. In contrast, the crystal has the highest energy when the
magnetization points along its *hard axis* direction. In cubic crystals the easy axis directions are generally <100> or <111>. The magnetization saturation can be achieved with quite low magnetic field along the easy axis direction of a material. Figure 2-6 illustrates schematic magnetization curves for Ni single crystal, with the field applied along its easy (111) and hard (100) axis directions. In both cases the same saturation magnetization is obtained, but for magnetizations along the hard axis, much larger magnetic field is required to reach the saturation value.

![Figure 2-6 Schematic magnetization curve for Ni single crystal with the magnetic field applied along its easy (111) and hard (100) axes.](image)
When the applied magnetic field exerts a torque to deviate the magnetic spin from an easy axis, the spin-orbit coupling tends to rotate the orbit also. The orbits, however, are more strongly connected to the lattice, and therefore their rotation needs more energy than the rotation of spins. As a result, the energy needed to move the magnetization vector away from an easy axis direction can be expressed as a series expansion of the cosines of angles between the magnetization and the crystal axes:

$$E_K = K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2$$

where $K_1$ and $K_2$ are the magnetocrystalline anisotropy constants (in J/m$^3$) characteristic of the material, and the $\alpha$ is the angle cosine. The amplitude and sign of the magnetocrystalline anisotropy constants determine the direction of minimum anisotropy energy (easy axis). For $<100>$ easy axis (such as CoFe$_2$O$_4$), $K_1$ is positive, whereas $<111>$ (such as NiFe$_2$O$_4$) leads to negative $K_1$ values. The anisotropy constant decreases with increasing temperature and it drops slowly to zero at the Curie temperature.

The magnetic anisotropy governs the magnetization properties and can be induced by a demagnetizing field as the source of sample shape (shape anisotropy) and stresses (stress anisotropy) as well as the crystallographic texture (magnetocrystalline anisotropy).

**Shape Anisotropy**

Shape anisotropy is a result of the interaction of a magnetized material with its own demagnetization field which is related to the magnetostatic energy and not to spin-orbit coupling. Shape anisotropy is an important property in particles and thin films. In thin
films, shape anisotropy causes the magnetization to stay in-plane in order to minimize the
demagnetizing field. The surface arrangement, however, tends to cause the magnetic
moments to align perpendicular to the surface (surface anisotropy). The competition between
the shape and the surface anisotropy can lead to reorientation transitions as a function of the
film thickness  

\[ E = \frac{3\sigma \lambda_s \cos^2 \theta}{2} \]  

\[ K_{u\sigma} = \frac{3\sigma \lambda_s}{2} \]  

**Stress Anisotropy**

Stress in the lattice structure of a magnetic material can affect the ability of the orbitals to
rotate and reorientate under the applied magnetic field. Stress anisotropy also known as
magnetoeelastic anisotropy is related to magnetostriction and can be explained on the basis of
the spin-orbit coupling  

In thin films, stress anisotropy can rise from stresses induced in the film due to lattice
mismatch or thermal expansion differences between the film and substrate. The
magnetoeastic energy produced due to the stress and resulting value of strain
(magnetostriction, \( \lambda \)) in the film is expressed in following equation  

\[ E_{me} = -3\sigma \lambda_s \cos^2 \theta / 2 \]  

where \( \lambda_s \) is an isotropic magnetostriction coefficient and \( \theta \) is the angle between the
magnetization M and \( \sigma \). Therefore, uniaxial anisotropy can be created with a releavnt stress-
induced anistropy constant given by  

\[ K_{u\sigma} = 3\sigma \lambda_s / 2 \]  

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\[ K_{u\sigma} = 3\sigma \lambda_s / 2 \]
In magnetic thin films, shape and stress anisotropies are of equal importance as the magnetocrystalline anisotropy. Therefore, for magnetic thin films, the overall magnetic anisotropy can be expressed as the sum of all contributions \(^3,6,9\):

\[ K_u = K_{sh} + K_{u\sigma} + K_{ui} \]  

\text{eq. 2.6}

where \(K_{sh}\) is the shape anisotropy, \(K_{u\sigma}\) is the stress anisotropy and \(K_{ui}\) is the magnetocrystalline anisotropy.

2.1.4 Magnetostriction

Magnetostriction in a ferro/ferrimagnetic material is defined as a change in material dimension due to magnetization. The change in length can be positive along the direction of magnetization (e.g. Fe) or negative (e.g. Ni). Although the length change is very small for most magnetic materials, it is sufficient to influence the domain structure and affect the magnetization properties \(^6\).

Magnetostriction, similar to the other intrinsic magnetic properties of the materials such as spontaneous magnetization and magnetocrystalline anisotropy, has origins in atomic scale magnetism \(^4\). It is mainly the result of spin-orbit coupling of valence electrons, which is also responsible for magnetocrystalline anisotropy \(^3\). Any change in spin direction results in orbital orientation changes due to spin-orbit coupling. Since the orbits are strongly connected to the crystal lattice, changes in orbital orientation cause a spontaneous deformation in the lattice in the direction of domain magnetization \(^4,8\). Hence it can be said that most of the
magnetostrictive change in length occurs during the orbital orientation as shown schematically in the Figure 2-7 3.

![Figure 2-7 Schematic of magnetostriction caused by domain rotation in a magnetic material 3.](image)

The oval lines show the electron clouds belonging to each atom and the arrows represent the magnetic moment per atom. Above $T_c$, the material is paramagnetic with random orientation of the magnetic domains. If the spin-orbit coupling is sufficiently strong enough, below $T_c$ the spins rotate and the electron clouds point into a particular orientation dictated by the crystal anisotropy (easy axis). If a strong magnetic field is applied vertically, the spins and the electron cloud rotate and the magnetic domain of which these electrons are a part change in dimension magnetostrictively by an amount of $\frac{\Delta L}{L}$ 3 (Figure 2-8).
Figure 2-8 Schematic shows the change in length for a piece of ferromagnetic material due to applying a magnetic field.

By definition, the saturation magnetostriction constant ($\lambda_s$) is the strain, i.e., the fractional change in length $\Delta L / L$ produced by a saturating magnetic field, and is dimensionless. The value of magnetostriction depends on the applied field and it changes typically as shown in Figure 2-9 in a substance with positive magnetostriction constant $^3$.

Figure 2-9 Dependence of the magnetostriction on the applied magnetic field $^3$. 
Resulting from the magnetic anisotropy, magnetostriction is also anisotropic. Since both results from spin-orbit coupling, there is correlation between the values of the anisotropy constant $K_1$ and the magnetostriction, $\lambda_s$. Typical values of saturation magnetostrictions and anisotropy constants for different ferrites are given in Table 2-1.

Magnetostriction Measurement

To measure the magnetostriction properties of bulk materials, either mechanical and/or optical levers to magnify the magnetostrictive strain or electrical-resistance strain gauge are used. However, thin film samples present challenges in the measurement of magnetostriction due to their bonding to a nonmagnetic substrate and the resulting clamping effect. If the substrate is sufficiently thin, a change in film dimension may produce a measurable curvature in the substrate, from which the magnetostrictive strain can be deduced.

2.2 Ferrites

Ferrites are the most important magnetic oxides with high electrical resistivity making them suitable for many applications including memory storage, spintronics and high frequency devices. The magnetic ferrites fall mainly into two main groups with different crystal structures:

1. Cubic, with general chemical formula $\text{MFe}_2\text{O}_4$ (M is a divalent metallic cation, e.g. $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Mg}^{2+}$, ...). $\text{CoFe}_2\text{O}_4$ is a hard magnet, while all other cubic ferrites are magnetically soft.
2. Hexagonal, the most important in this group are strontium and barium ferrites (BaO.6 Fe₂O₃ and SrO.6 Fe₂O₃), which are magnetically hard.

2.2.1 Crystal Structures of Spinel Cubic Ferrites

The spinel ferrites are a very large category of over 140 oxides and 80 sulfides which possess similar crystal structure to natural spinel MgAl₂O₄\(^{2,8}\). They are predominately ionic with general chemical formula of MX₂O₄ (M and X are divalent and trivalent metallic ions) and space group of F3dm \(^{8}\). Each unit cell contains eight formula units (i.e. 32 O\(^{2-}\) ions, 16 X\(^{3+}\) ions, and 8 M\(^{2+}\)) with a cubic close-packed (FCC) array of oxygen atoms in which one-half of the octahedral (B sites) and one eighth of tetrahedral sites (A sites) (Figure 2-10) are occupied by metallic cations \(^{8}\). Hence in a unit cell, 8 of available A sites and 16 of the available B sites are occupied by the cations \(^{10}\).
Figure 2-10 One-eighth portion of a unit cell of cubic spinel. The O\(^{2-}\) ions in an FCC arrangement are shown in black. The metallic ions (yellow) are interstitially located in tetrahedral (A) and octahedral (B) sites.

The physical properties of spinels are governed not only by the type of cation in the lattice, but also by their distribution over the available crystal sites\(^8\). In a normal spinel structure, divalent M and trivalent X cations occupy the octahedral and tetrahedral sites, respectively. In an inverse spinel, the trivalent cations are split between octahedral and tetrahedral sites and the divalent cations are positioned at the remaining octahedral sites. In many cases, however, intermediate cation distributions have been observed. In inverse spinel ferrites, octahedral site occupancy by two kinds of cations (divalent and trivalent) can lead to long-range order of two ionic sublattices on octahedral sites\(^8\).
2.2.2 Ferrimagnetic Spinel Cubic Ferrites

The most important magnetic spinels are oxides MFe$_2$O$_4$ (e.g. NiFe$_2$O$_4$, CoFe$_2$O$_4$, and LiFe$_2$O$_4$) with magnetic ordering at room temperature and inverse spinel cubic structure. The magnetic moments per unit formula equal that of the M$^{2+}$ ion because the Fe$^{3+}$ ions are evenly distributed among the A and B interstitial sites. Hence, their magnetic properties result from the magnetic moments of the metal ions (M$^{2+}$). This can be explained by antiferromagnetic coupling between the spin moments of the metallic cations in the octahedral and tetrahedral sites through indirect exchange interactions. Direct exchange interactions between the cations (ferromagnetic) is negligible because of their separation by oxygen anions as well as the large cation-cation distance.

Hence, because of the geometry of orbitals involved, the superexchange interaction via two extra 2P electrons of the O$^{2-}$ and 3d spins of two neighboring metal cations take place. This superexchange coupling between octahedral and tetrahedral cations or A-O-B interactions with an angle of 135° is the strongest and most dominant interaction in inverse spinel ferrites. As a result of uncompensated antiferromagnetic coupling in the unit cell, the spinels show ferrimagnetic behavior. This indirect exchange coupling in spinels was observed for the first time by neutron diffraction. Therefore, it can be generally concluded that the spontaneous magnetization of spinels can be estimated on the basis of their composition, cation distribution and the relative strength of the possible interactions. The magnetic characterization of some of the most important spinel ferrites are presented in Table 2-1.
Table 2-1 Magnetic properties of some of the basic spinel ferrites\textsuperscript{1-3,8,10}.

<table>
<thead>
<tr>
<th></th>
<th>(\text{NiFe}_2\text{O}_4)</th>
<th>(\text{CoFe}_2\text{O}_4)</th>
<th>(\text{Fe}_3\text{O}_4)</th>
<th>(\text{MgFe}_2\text{O}_4)</th>
<th>(\text{MnFe}_2\text{O}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_{B,\text{th}})</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>(n_{B,\text{exp}})</td>
<td>2.3</td>
<td>3.7</td>
<td>4.1</td>
<td>1.0</td>
<td>4.6</td>
</tr>
<tr>
<td>(\Delta (10^3 \text{kg/m}^3))</td>
<td>5.38</td>
<td>5.29</td>
<td>5.24</td>
<td>4.52</td>
<td>5.00</td>
</tr>
<tr>
<td>(\rho (\text{\Omega m}))</td>
<td>(10^4)</td>
<td>(10^5)</td>
<td>(10^5)</td>
<td>(10^5)</td>
<td>(10^2)</td>
</tr>
<tr>
<td>(T_c (^\circ \text{C}))</td>
<td>585</td>
<td>520</td>
<td>585</td>
<td>440</td>
<td>330</td>
</tr>
<tr>
<td>(K_1 (10^5 \text{erg/m}^3))</td>
<td>-0.62</td>
<td>20</td>
<td>-1.1</td>
<td>-0.25</td>
<td>-0.3</td>
</tr>
<tr>
<td>(\lambda_s (10^{-6}))</td>
<td>26</td>
<td>110</td>
<td>40</td>
<td>-6</td>
<td>-5</td>
</tr>
<tr>
<td>(M_s (0\text{K}))</td>
<td>300</td>
<td>475</td>
<td>510</td>
<td>140</td>
<td>560</td>
</tr>
<tr>
<td>(M_s (300\text{K}))</td>
<td>270</td>
<td>425</td>
<td>480</td>
<td>120</td>
<td>400</td>
</tr>
</tbody>
</table>

\(n_{B,\text{th}}\) and \(n_{B,\text{exp}}\) are the calculated and experimental magnetic moments at 0K per unit formula (Bohr magneton). \(T_c\) is the Curie temperature. \(\delta\) and \(\rho\) are mass density and electrical resistivity, respectively. \(K_1\) is the anisotropy constant. \(\lambda_s\) and \(M_s\) are the saturation magnetostriction and magnetization, respectively\textsuperscript{10}.

Due to magnetic properties of cubic spinel ferrite (e.g. \(\text{CoFe}_2\text{O}_4\), \(\text{NiFe}_2\text{O}_4\), ...) at room temperature, to date, many studies have been conducted to characterize them in bulk, powder and, thin and thick film forms.
2.2.3 Nickel Ferrite (NiFe$_2$O$_4$)

With moderate dielectric properties, Fe$^{3+}$[Ni$^{2+}$Fe$^{3+}$]O$_4$ (NFO) has an inverse spinel structure and room temperature ferrimagnetic behavior. NFO is a soft magnetic spinel ferrite with high permeability, low eddy current losses, and a wide band gap (above 3 eV). These properties, accompanied with high thermal and chemical stability, make NFO particularly of interest for various technological applications such as high frequency magnetostatic devices, microwave applications such as circulators and phase shifters, magnetic recording devices, microwave acoustics and spintronics.

Based on the Néel ferrimagnetism, the saturation magnetization of NFO at 0 K can be calculated using the ionic moments of Ni$^{2+}$ and Fe$^{3+}$ in both A and B sites. Using 2 $\mu$B per Ni$^{2+}$ and 5 $\mu$B per Fe$^{3+}$, the calculated saturation magnetization of the complete inverted NiFe$_2$O$_4$ is 2 $\mu$B per formula.

Studies have investigated NFO, and NFO-Zn or Cu solid solutions in different forms, including bulk, nano particle, and films. Although for many applications it is of interest to leverage the large magnetic anisotropy that results from orienting films in the energetically favored magnetic direction, few systematic studies on oriented NFO thin films have been reported, and the only studies on epitaxial or textured films involve films prepared by pulsed laser deposition (PLD), DC sputtering, or chemical vapor deposition (CVD), while studies on ferrite thin films such as NiFe$_2$O$_4$ and CoFe$_2$O$_4$ deposited by chemical solution deposition (CSD) have resulted only in randomly oriented polycrystals.
Chemical Solution Deposition (CSD) of NiFe$_2$O$_4$ Thin Films

CSD offers significant advantages relative to other thin film deposition techniques and thus attracted interest for thin films production. CSD is particularly suited for the control of purity and stoichiometry in films; in addition, film deposition can take place in non-vacuum environments and hence potentially less expensive set-up. Moreover, the use and synthesis of molecular precursors usually leads to enhanced reactivity and densification at greatly reduced temperatures. The latter advantage has been the driving force for the integration of ferroelectric materials. However, the most important advantage of CSD over other deposition methods is the ability to tailor the microstructure of the deposited films.

In CSD, inorganic or organic metal compounds are used as raw ingredients. These compounds are hydrolyzed in aqueous or organic solvents and condensed to form inorganic polymers composed of M--O--M bonds (M is the metallic cation) $^{61}$.

To date, few chemical routes have been reported in the literature to grow NFO thin films. Bae et al. $^{35}$ used acetate and nitrate procurers and ethanol solvent to grow nickel-zinc ferrite thin films on yttria stabilized zirconia buffered Si(100). Mohallem et al. $^{37}$ employed nitrate precursors to grow NiFe$_2$O$_4$/SiO$_2$ thin film composites. Sedlar et al. $^{36}$ also used nitrate precursors and 2-methoxyethanol (2-MOE) solvent to grow NFO thick films. Nitrate precursors are employed by Tsuchiya et al. $^{33}$ but glycerol, formamide and HCl were used as solvent. None of these studies reported any preferential growth (crystallographic texture) in the NFO (or solid solution NFO) thin films.
2.3 Crystallographic Texture Evaluation

Crystallographic texture is defined as a preferred orientation of crystallites in a polycrystalline material. This intrinsic characteristic of metals, ceramics, rocks and polymers strongly affects anisotropic properties such as mechanical strength, electrical and thermal conductivity, magnetic, ferroelectric and optical properties. Many methods are used to determine the preferred crystallographic orientation in a material. Geologists have used optical methods to study the texture in rocks using a microscope equipped with a universal stage to measure the orientation of morphological and optical directions in individual grains. Today, diffraction techniques using Bragg’s law are most widely used to measure the crystallographic preferred orientation. In this method, an X-ray diffractometer with a pole figure goniometer is employed. In addition, electron diffraction is used to evaluate the crystallographic texture in a much smaller and limited area of the specimen.

2.3.1 XRD θ-2θ Scan

Typically, the initial estimates of the presence of a preferential orientation can be obtained from the relative intensities of Bragg peaks in a conventional θ-2θ X-ray diffraction (XRD) scan. The relative intensity of the stronger peaks relative to peaks from a random powder specimen identifies a direction of preferred crystallographic orientation that is normal to the diffracting planes for that peak. However, peak intensities in θ-2θ XRD scans only provide information on diffracting planes that are parallel (or in very small divergence) to the sample.
surface. Hence it does not provide any information on the texture in the grains at an angle with the sample surface \(^{63}\).

2.3.2 XRD Pole Figure Scan

A pole figure is a stereographic projection of a certain plane in the specimen. It gives the statistical probability of a given crystallographic orientation (fixed Bragg angle, \(2\theta\)) as a function of relative orientation of the specimen with respect to the diffractometer \(^{64,65}\). Pole figures can be considered as a planar projection of the intersections of the hkl plane’s normal with an imaginary hemisphere above the sample surface.

A pole figure collects signals from many crystals and averages over a large volume of crystallites. To determine the orientation of a given lattice plane, hkl, the detector is first set to the proper Bragg angle, \(2\theta\) of the diffraction peak of interest. The sample is then rotated in plane for 360° (\(\varphi\) angle) and tilted (\(\psi\) angle) in a goniometer until the lattice plane hkl is in the reflection condition (fulfilling Bragg’s law) (Figure 2-11) \(^{62}\). The sample must be rotated to get diffraction from planes which are not parallel to the sample surface.

![Figure 2-11 Sample rotation configuration in an X-ray pole figure setup.](image-url)
A randomly oriented sample, i.e. uniform dispersion of orientations, results in the same intensity in all directions, and hence there will be no feature in the obtained pole figure. In a textured sample, the poles group together. In a sample with fiber texture (uniaxial texture), rotational symmetry will be observed around fiber direction, i.e. the texture can be identified by the occurrence of circles centered around the origin of the pole figure. In a single crystal or an epitaxial film, only one family plane is diffracted and hence the pole figure will show discrete symmetrical spots from the diffracted plane (Figure 2-12).

Figure 2-12 Pole figures of a single crystal, fiber textured and randomly oriented specimen

(Rigaku Inc.)

2.3.3 XRD $\phi$-scanning

In $\phi$-scanning, the intensity of a single peak as a function of sample rotation is recorded. The obtained data can be used to quantify the texture and also in thin films it leads to the film
crystallographic orientation with respect to the substrate. Moreover, it can be employed to distinguish between overlapping substrate and film peaks 63.

2.3.4 TEM Electron Diffraction

Despite the pole figure, the TEM offers excellent opportunities to study textural details in very small area inside the sample 62. The outstanding advantage of texture analysis using transmission electron microscopy over X-ray diffraction is that a selected specimen region can both be imaged at high resolution and be investigated for its grain orientations.

If a polycrystalline sample is crystallographic textured, the electron diffraction pattern rings become arcs. In the case of epitaxial thin films, the epitaxial relationship between the film and the substrate also can be evaluated using the electron diffraction pattern.
2.4 Multiferroic Materials

Multiferroics are a class of multifunctional materials that show the coexistence of two or more ferroic orders, such as ferroelectricity, ferromagnetism, and ferroelasticity. Recently the classification of a multiferroic has been broadened to include antiferroic order as well. The coupling interaction between different orders can result in an additional functionality, such as magnetoelectricity (Figure 2-13). For clarification, different ferroic orders are defined in Table 2-2.

<table>
<thead>
<tr>
<th>Ferroelectrics</th>
<th>Possess a spontaneous stable polarization which can be switched hysteretically by an applied electric field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antiferroelectrics</td>
<td>The ordered dipole moments cancel each other completely within each crystallographic unit cell</td>
</tr>
<tr>
<td>Ferromagnetics</td>
<td>Exhibit a spontaneous magnetization that is stable and can be switched hysteretically by an applied magnetic field</td>
</tr>
<tr>
<td>Antiferromagnetics</td>
<td>Possess ordered magnetic moments that cancel each other completely within each magnetic unit cell</td>
</tr>
<tr>
<td>Ferroelastics</td>
<td>Display a spontaneous deformation that is stable and can be switched hysteretically by an applied stress</td>
</tr>
</tbody>
</table>

2.4.1 Magnetoelectric Materials

In magnetoelectric (ME) materials, application of an AC or DC magnetic field results in a dielectric polarization (direct ME effect, $\text{ME}_H$) and an AC or DC external electric field induces magnetization (converse ME effect, $\text{ME}_E$). It can be said that the
magnetoelectricity is a product property of the interaction between the magnetic and electric dipoles.

Figure 2-13 Relationship between multiferroic and magnetoelectric materials. 

There is rapidly growing interest in ME materials due to their potential use in many applications, including detection probes of AC and DC magnetic fields, transducers in electromagnetic pickups, and recording heads. In addition, the hysteretic nature of the ME effect makes them potential candidates for use in new generation of memory devices, where data can be written electrically and read magnetically. Intrinsic magnetoelectricity is observed in single phase materials, such as Cr$_2$O$_3$ or can be obtained in strain-mediated composites.
Single Phase ME Materials

Intrinsic magnetoelectricity in single phase materials is a result of coupling between two concurrently present orders \(^{81}\). For the first time it was observed in Cr\(_2\)O\(_3\) \(^{82}\) and to date several different compounds are studied, motivated by their potential applications in information storage, spintronics and multiple-state memories \(^{71}\). BiFeO\(_3\) is one of these materials which due to its relatively high Curie and Neel temperatures is most widely investigated. However, this material is G-type antiferromagnetic or only very weak ferromagnetic \(^{71}\).

Aside to their low Curie temperature, single phase materials have not shown high ME coupling response which hinders their practical applications.

Magnetoelectric Composites

Alternatively, and with greater design flexibility, the strain-mediated ME composites couple ferroelectric and ferromagnetic phases; such composites can produce a ME response at room temperature that can be several orders-of-magnitude larger than single phase ME materials \(^{68,71}\). The magnetoelectric response in strain-mediated ME composites is created through the coupling in materials where the magnetic and electrical order parameters arise in separate but intimately connected phases \(^{66}\).

According to the definition, the composite ME effect is a product property of the magnetostrictive effect (magnetic/mechanical effect) in the magnetic phase and the
piezoelectric effect (mechanical/electrical effect) in the ferroelectric phase, as shown in following equations \(^{71}\);

Direct ME response, \( ME_H = \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electric}} \)

Converse ME response, \( ME_E = \frac{\text{electric}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}} \)

Similar to the other composites, in ME composites two coupled phases need to be chemically compatible and stable \(^{83}\). While many factors influence the ME behavior of such a composite, to obtain a high ME response, a ferroelectric phase with a high piezoelectric coefficient and a ferromagnetic phase with large magnetostrictive response are preferred. To sustain the applied/generated electrical field in a direct/converse ME composites, it is also beneficial for the MS phase to have a high electrical resistivity. Moreover, and perhaps more importantly, to optimize the strain coupling, the two phases need to have strong mechanical coupling \(^{83}\). Magnetoelectric composites offer greater flexibility in material selection and in geometry, and therefore their full potential has yet to be determined.

- **Materials for the ME Composites**

For the first time, Van Suchtelen \(^{84}\) proposed the concept of the ME composite and since then, the ME composites have got tremendous attention in different configurations and made from large number of combination of ferroelectric and magnetic materials. The most studied ferroelectric and magnetic phases in ME composites are summarized in Table 2-3.
Table 2-3 Mostly studied materials to fabricate the ME composites

<table>
<thead>
<tr>
<th>Ferroelectric phase</th>
<th>Magnetic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pb}[\text{Zr}<em>x\text{Ti}</em>{1-x}]\text{O}_3$ (PZT)</td>
<td>$\text{Tb}<em>x\text{Dy}</em>{1-x}\text{Fe}_2$ (Terfenol-D)</td>
</tr>
<tr>
<td>$\text{Pb(Mg,Nb)}\text{O}_3$-$\text{PbTiO}_3$ (PMN-PT)</td>
<td>$\text{CoFe}_2\text{O}_4$ (CFO)</td>
</tr>
<tr>
<td>$\text{PbTiO}_3$</td>
<td>$\text{NiFe}_2\text{O}_4$ (NFO)</td>
</tr>
</tbody>
</table>

Ferroelectric Materials

For the past few decades, ferroelectric materials have received a great amount of interests because of their various uses in many applications such as nonvolatile ferroelectric random access memories (NVFRAM), dynamic random access memories, sensors and microactuators. A ferroelectric crystal possesses spontaneous polarization vector in the absence of an external electric field, and the spontaneous polarization can be switched between those orientations by an electric field. The most extensively studies ferroelectrics are the perovskite with a general formula of $\text{ABO}_3$, where A is a divalent or trivalent cation, and B is a tetravalent or trivalent cation.

*Lead zirconate titanate $\text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$*

$\text{Pb(Zr}_{1-x}\text{Ti}_x)\text{O}_3$, or PZT, is a ferroelectric with perovskite structure which is widely used in piezoelectric actuators and sensors due to its superior piezoelectric coefficient at room
temperature. This material possesses a large piezoelectric coefficient and permeativity. These properties combined with its ease in processing, availability and relatively low costs, make it one of the most widely used ferroelectric material.

According to the phase diagram, the strongest room temperature piezoelectric properties occur in the vicinity of a morphotropic phase boundary (MPB) between tetragonal (T) and rhombohedral (R) ferroelectric phases near x~0.50 (Figure 2-14).

![Figure 2-14 Simple Pb(Zr_{1-x}Ti_x)O_3 phase diagram](image)

In the perovskite structure of PZT, Pb atoms sit at cube corner positions, Zr or Ti atoms randomly sit at body center positions and O atoms sit at the face centered positions (Figure 2-15).
Various composite geometries have been investigated, including bulk, thin film and nanostructure composites. The most common ME bulk composites include laminated composites with 2-2 connectivity, 0-3 type particulate composites, and 1-3 type rod/fiber composites (Figure 2-16). Although 0-3 type particulate bulk composites are expected to show a high ME response, their performance remains much lower than theoretically predicted due to the inherent preparation challenges, including those associated with high processing temperatures resulting in possible chemical reactions between the PE and MS phases, difficulty in controlling the connectivity, and their tendency to have a relatively high density of structural defects. The presence of defect such as dislocations, voids and cracks can cause preferential electrical leakage paths resulting in a
reduced overall ME response \(^{71,75,83,183}\). In addition, to overcome the leakage problem associated with low electrical resistivity of ferrite particles, well dispersed MS particles in the PE matrix are desired, yet preparation of composites with this geometry remains a significant challenge \(^{71}\).

\[
\text{Figure 2-16 Schematic of different configurations of composites (a) 0-3 type particulate composites, (b) 1-3 type rod/fiber composites (c) 2-2 type laminated composites.}
\]

In contrast to the 0-3 composites, bulk, laminated (2-2) composites show higher ME coefficients due to improved PE/MS interfaces that result in enhanced mechanical coupling and reduced electrical leakage currents. The low resistivity of the MS phase can be overcome by sandwiching the MS layer between the PE layers \(^{71}\). The crystallinity of each phase is improved by optimizing their thermal processing separately, which is facilitated by separately annealing the PE and MS phases \(^{83}\). Each layer’s thickness can be controlled independently, and hence the volume fraction of each phase can be adjusted without affecting the active interfaces and increasing the leakage current \(^{179}\). Furthermore, PE and MS thin films can be coupled at the atomic level epitaxially \(^{71}\). From the applications perspective,
laminated thin film composites are directly applicable to high density memory devices and MEMS. Therefore, recent studies have focused mostly on laminated thin film composites consisting of alternating PE and MS layers. A variety of ME multilayer thin film composites have been reported. Although CFO has a larger magnetostrictive coefficient, NFO is thermodynamically extremely stable and does not react with PZT even at temperatures as high as 1050 °C. In addition, strong adhesion between NFO and PZT enhances the mechanical coupling. NFO is magnetically softer than CFO and has higher electrical resistivity. Pure NFO has been mostly used as the magnetostrictive phase in bulk ME composites. Zn-doped NFO/PZT thick films have been reported, however, where the addition of Zn increased the magnetization at the expense of lowering the Curie temperature. No systematic investigations on the properties of thin film NFO/PZT multilayered composites have been reported, nor have microstructural studies of thin- or thick-film NFO/PZT multilayers.

2.4.2 ME Properties Measurement

The ME coefficient ($\alpha_{ME}$) is calculated by equation:

$$\alpha_{ME} = \frac{\delta E_{AC}}{\delta H_{AC}}$$

There are three methods of measuring ME output:

**Static** - In the static method, an electrometer with high input impedance is used to measure the ME output (charge or voltage) as a function of increasing magnetic field. In this method,
there is a high possibility of charge accumulation at the grain boundaries while poling. The
carries move towards the electrodes during the measurement. The discharge of the charges
needs quite a lot of time, before actually the final output is stabilized. The accumulated
charges may lead to erroneous conclusions in some materials 76.

Quasi- static-The quasi-static method leads to more precise data and involves a time varying
DC magnetic field and a high impedance electrometer. The output is measured as a function
of time. This technique was used by Rivera (1994) in single crystal boracites and Ye et al
(1994) in Cr₃B₇O₃Cl. But similar to the static method, this method cannot be employed for a
polycrystalline ME material due to the charge build up at the grain boundaries 76.

Dynamic-Using the setup shown in Figure 2-17, the output ME voltage is measured using a
bias AC magnetic field, i.e. the measurement is carried out with a time varying DC magnetic
field in the presence of an AC field. The applied bias AC magnetic field prevents the charges
from moving towards the electrodes since a suitable signal with an appropriate frequency is
used where the polarity of the signal changes with time. 76.
The basic equations necessary to evaluate ME coefficients from the voltage are given below. When a DC magnetic field is applied, in a polycrystalline material, the ME output voltage (V) can be given by the following equation,

\[ V \propto (\alpha H + \beta H^2) \]  

where \( \alpha \) and \( \beta \) are the coefficients of linear and quadratic components of ME. Suppose that if an AC field \( h_0 \) is superimposed over the DC field \( H_0 \), then the effective field is

\[ H = H_0 + h_0 \sin(\omega t) \]  

A lock-in-amplifier tuned to the frequency \( \omega \) (\( \omega = 2\pi f \)) measures the output ME signal. Then we can write,
\[ V \propto (\alpha + \beta H_0) h_0 = \alpha^* (H_0) h_0. \] \hspace{1cm} \text{eq. 2.10}

When \( H_0 \) is zero, it is possible to find out the linear term \( \alpha \) and hence the second-order term \( \beta \) is evaluated in the presence of DC magnetic field. When \( H_0 \) is not zero, the above equation shows that \( \alpha \) varies with \( \beta \), giving rise to a pseudo-linear coefficient \( \alpha^*(H_0) \).  

2.5 References


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CHAPTER 3
RESEARCH METHODOLOGY

3.1 Solution Preparation

3.1.1 NiFe₂O₄

NiFe₂O₄ (NFO) solutions with 0.5 and 0.2 molarity are made by dissolving separately nickel acetate tetrahydrate (Ni(CO₂CH₃)₂.4H₂O) and ferric nitrate nonahydrate (Fe(NO₃)₃.9H₂O) in a 2-methoxyethanol (CH₃OCH₂CH₂OH) solvent (all supplied by Sigma Aldrich, Inc., St. Louis, MO). Each solution is stirred for 2 hours at 65 °C by inserting the flasks in a heated oil bath and subsequently mixed at room temperature for 10 minutes. The flowchart of the procedure is shown in Figure 3-1.

![Flowchart of NFO solution preparation](image)

Figure 3-1 Procedure of NFO solution preparation.
The pseudo-binary phase diagram of Fe$_2$O$_3$-NiO in air is shown in Figure 3-2. To prevent any formation of iron oxide and have a pure NiFe$_2$O$_4$, the stochiometric ratio should be controlled carefully.

![Figure 3-2 The pseudo-binary phase diagram of Fe$_2$O$_3$-NiO in air](image)

3.1.2 Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$

A 0.4 molar Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (PZT) solution is made with 10% excess Pb with respect to stoichiometry, in order to compensate for its volatility at high temperature. The procedure is illustrated in Figure 3-3. Lead acetate trihydrate (Pb(CH$_3$CO$_2$)$_2$·3H$_2$O) is dissolved in the 2-methoxyethanol solvent under an Ar atmosphere at 70 °C. The solution is then dehydrated under vacuum until a semidry powder remains. A room temperature mixture of zirconium n-propoxide (Zr(OCH$_2$CH$_2$CH$_3$)$_4$) and titanium iso-propoxide 99.999% (Ti[OCH(CH$_3$)$_2$]$_4$) in the 2-methoxyethanol solvent is added (all supplied by Sigma Aldrich, Inc., St. Louis, MO).
The entire solution is then mixed for 2 hours under an Ar atmosphere at 120 °C. Subsequently, the solution is vacuum distilled and 2-methoxyethanol is added until the desired solution molarity is achieved.²

3.2 Thin film preparation

NFO and PZT thin films are prepared using chemical solution deposition as shown schematically in Figure 3-4. CSD involves three steps: spin coating, pyrolysis and annealing. This cycle is repeated to achieve the desired thickness.

Figure 3-3 Procedure of PZT solution preparation.
Spin coating is carried out at speeds ranging from 2000 rpm to 8000 rpm using a spin coater (WS-400-6NPP-lite from Laurell Technologies Corporation). An image of the spin coater is shown in Figure 3-5.
The solution is poured on the substrate using a syringe and needle. The wafer is then rotated on a spinning wheel at high speed so that centrifugal forces push the excess solution over the edge of the wafer, and a residue on the wafer remains due to surface tension. Spin coating deposition can be divided to four stages: deposition, spin-up, spin-off and evaporation. In the deposition stage, liquid is dispensed on the surface. In the spin-up stage, centrifugal force drives the liquid to flow radially outward. In the spin-off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, because of greater flow resistance and higher concentration of non-volatile components, the rate of removal of excess liquid slows down. Lastly the evaporation takes over as the primary mechanism of thinning. After deposition, the films are pyrolyzed in air using a hotplate for 1 min to remove the solvent and form an amorphous layer. The films are consequently annealed in air to crystallize and form the NFO structure.

DC sputtering is used to deposit a Pt layer which serves as an intermediate and top electrode.

Substrates

$Si/SiO_2$

The silicon substrates are provided by cutting a single side polished Si (100) wafer with 500 μm thickness supplied by University Wafer Company. TEM studies showed that the Si has about 5 nm-thick SiO₂ layer, naturally formed.
Si/SiO₂/TiOₓ/Pt(111)

The platinized silicon substrates are supplied from MEMS and Nanotechnologies Company. The structure of the substrates includes Si (100)/SiO₂/TiOₓ (111)/Pt(111) as shown schematically in Figure 3-6.

\[ \text{Figure 3-6 Structure of the platinized silicon substrates} \]

\[ \text{Si} \quad \text{SiO}_2 \quad \text{TiO}_x \quad \text{Pt} \]

\[ \text{500 nm} \quad \text{50 nm} \quad \text{100 nm} \]

\[ \alpha-\text{Al}_2\text{O}_3 \text{ (sapphire)} \]

Single side-polished corundum alumina (\( \alpha-\text{Al}_2\text{O}_3 \)) substrates are provided from University Wafer company in two different orientations, c-plane (0001) and R-plane (1102) with thickness of 430 μm. The schematic of the lattice structure and the crystallographic planes of the sapphire is illustrated in Figure 3-7.
Before each deposition, all substrates are cleaned using organic solvents (methanol, acetone and isopropyl alcohol) followed by heating on hotplate at 400 °C for 1 minute to remove all organic contamination and condensed water.

3.3 Characterization

3.3.1 DTA/TGA

Thermogravimetric analysis and differential thermal analysis are performed on prepared NFO solution in a STA 6000 analyser (Perkin Elmer) from 40 to 800 °C with a heating rate of 2 °C/min in air.
3.3.2 Conventional 0-2θ XRD

Conventional 0-2θ XRD scan is employed to characterize the phase formation and preferential growth of the films using Cu Kα radiation (λ=1.5418 Å) in a Rigaku DMax and Smartlab X-ray diffractometer at room temperature with a step size of 0.02 degrees and dwell time of 1 second.

3.3.3 Pole Figure XRD

The in-plane orientation of the films is evaluated by pole figure XRD in a Panalytical Empyrean X-ray diffractometer with a pyrolytic graphite monochromator. The pole figure XRD for χ=0 to 89° (tilting angle) is performed on the NFO (222) and (440) planes at 2θ=37.3° and 63.2°, respectively.

3.4 Microstructural Studies

3.4.1 Scanning Electron Microscopy (SEM)

Top surface and cross-sectional views of the thin films are examined using a back-scattered electron detector in a field emission SEM (Zeiss Ultra 60) with an electron beam of accelerating voltage of 5 kV. SEM cross-sectional samples are prepared by cleaving with a diamond scriber and sputtering a 15 nm layer of Au onto the sample to decrease surface charging during imaging.
3.4.2 Helium Ion Microscopy (HIM)

Cross-section and top-surface film microstructures are examined in a Zeiss Orion Plus helium ion microscope (HIM).

3.4.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is performed on the top surface and cross-section of the films in a JEOL 2000FX and a JEOL 2010F.

TEM Sample preparation

TEM samples are mechanically polished in a Multiprep system (Allied High Tech Inc.) followed by a low angle-low energy cryogenic ion milling.

To prepare the cross-sectional sample, using a specific grade of epoxy (M-bond 610), two pieces of cut samples are glued together as shown schematically in Figure 3-8.
Figure 3-8 Schematic of a sample prepared for cross sectional view of a film and a prepared specimen.

To polish both sides of the samples, diamond lapping films are used in different grits (Figure 3-9).

Figure 3-9 Diamond lapping films from different grit/color (from Allied website)
After the sample becomes sufficiently thin (below 30 µm), it needs to be wedged to get a thin edge on the sample. The prepared sample needs to be further polished more using ion milling as a supplementary method.

3.4.4 Secondary Ion Mass Spectroscopy (SIMS)

Elemental depth profiles of the thin films are analyzed by secondary ion mass spectroscopy (SIMS) using a Cameca IMS 6f. A primary beam of O\(^{2+}\), with beam energy of 10 keV, is rastered over a 180 × 180 µm\(^2\) region on the top surface of samples and the secondary ion signals are collected over the area with 60 µm diameter in the center.

3.4.5 Atomic and Magnetic Force Microscopy (AFM and MFM)

Topography of the top surface of thin films is studied in nano-scale resolution using atomic force microscopy (AFM). By changing the tip and scanning mode, various forces can be imaged, such as piezoresponse force microscopy (PFM) and magnetic force microscopy (MFM) which can be used to image ferroelectric and ferromagnetic domains respectively.

The basic structure of an AFM head is shown in Figure 3-10. A cantilever with a sharp tip at the end is used to detect the top surface of the sample. In proximity of the sample surface, forces between tip and sample lead to a deflection of the cantilever. The force is measured using laser spot reflected from top of cantilever.
In this study, the surface morphology and the magnetic domain structure of the grown ferrite films is studied in tapping and lift mode using a Cypher (Asylum Research). The MFM is done in interleave mode, which means that the tip scans the surface using a tapping mode first, and then the tip scans the same surface using lift mode. In tapping mode, the topography of the sample is recorded. In lift mode, the topography information is subtracted from the data; only the response of the magnetic tip to the magnetic signal is considered. If the magnetic tip is on top of a magnetic material, the vibration frequency of the tip changes due to the magnetic force between the tip and sample. Accordingly, the phase change of the tip in lift mode reflects the magnetic signal of the sample. The phase map of the lift mode in interleave is used as the MFM results.
3.5 Properties Measurement

3.5.1 Ferroelectricity

To assess ferroelectricity, the electrical polarization of the ferroelectric layer is evaluated using an RT66A ferroelectric testing unit by Radiant Technology with an applied electrical field up to 300 kV/cm.

The RT66A consist of an Arbitrary Waveform Generator (AWFG) to stimulate the sample and an electrometer to capture the electrical response by measuring the change in electrical charge of the sample over time. The size of the sputtered top electrodes is measured using a Nomarski microscope (differential-interference contrast) by Carl Zeiss.

3.5.2 Magnetization

Magnetization measurements are performed using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Magnetization hysteresis loops are measured at room temperature by applying a magnetic field parallel (in-plane) and normal (out-of-plane) to the plane of the films. The magnetization data are normalized to the volume of the magnetic layer and the substrate contribution is removed. The magnetization data for the out-of-plane direction is corrected for shape anisotropy using a demagnetization factor of $4\pi^4$. 
3.5.3 Magnetostriction

The magnetostriction is measured directly from the deformation in the sample under the magnetic field. For a rectangular substrate \((L \times W \times t)\) and the film with thickness \(d\), the substrate deformation caused by magnetostriction is deflection \(D\):

\[
D = \frac{3L^2 Sd(1-\nu_s)}{E_s t^2} \quad \text{eq. 3.1}
\]

Where, \(E_s\) and \(\nu_s\) are elastic modulus and Poisson’s ratio of the substrate, respectively. \(S\) is the magnetostrictive stress in the film, which is calculated from following equation;

\[
S = \frac{\lambda E_f}{1+\nu_f} \quad \text{eq. 3.2}
\]

Where \(E_f\) and \(\nu_f\) are the elastic modulus and Poisson’s ratio of the film and \(\lambda\) is the magnetostriction strain.

3.6 References


4.1 Motivation

Sol-gel is an extensively utilized technique to deposit oxide thin films not only because of its low cost and ease of processing but also because of the convenience in tailoring the films’ composition and structure. These advantages have led this technique to success in commercialization of oxide-based thin films \(^1\). Despite the advantages of sol-gel techniques over the others thin film deposition methods, including sputtering and chemical vapor deposition, however, the growth of NiFe\(_2\)O\(_4\) (NFO) thin films by chemical routes have not been reported in the literature and thus no systematic investigation of the microstructure and magnetic properties of NFO films prepared via chemical solution deposition has been performed.

In this chapter, randomly-oriented NiFe\(_2\)O\(_4\) thin films are grown onto Si substrates via a new chemical route. Microstructural and magnetic studies have been performed on the grown films to study the effect of the deposition and annealing conditions.

4.2 Approach

An NiFe\(_2\)O\(_4\) (NFO) solution with 0.5 molarity is prepared by the chemical procedure described in chapter 2. Thermogravimetric and differential thermal analysis are performed on the NFO solution from 40 to 800 °C with a heating rate of 2 °C/min in air.
NFO thin films are deposited onto Si (100) substrates using spin coating (2000 rpm × 30 sec). The deposited films are pyrolyzed on a hot plate and rapid thermally annealed. The room temperature θ-2θ XRD scan is employed to characterize the phase and crystallographic orientation of the deposited films at room temperature. The top surfaces and cross-sections of the thin films are examined using a back-scattered electron detector in a field emission SEM and TEM. The room temperature magnetic properties of the films are studied using a SQUID magnetometer. The magnetization data are normalized to the volume of the magnetic layer and the diamagnetic contribution of the Si substrate is removed.

4.3 Results and Discussion

4.3.1 Solution Characterization

Typical TGA and DTA curves are collected during heating of the 0.5 M NFO solution (Figure 4-1). The TGA curve exhibits two distinct weight loss steps at 100 °C and 325 °C. The DTA curve shows one endothermic peak and one sharp exothermic peak below 300 °C. These peaks are due to the solvent evaporation (CH₃OCH₂CH₂OH) and decomposition of the nitrate and acetate phases (the precursor compounds) and formation of amorphous clusters in the solution. The solvent loss is accompanied with weight loss below 350 °C. At temperatures higher than 350 °C, the sample weight remains constant; indicating that decomposition of long chain organic molecules is complete. There is no further weight loss but a broad exothermic peak is seen in the range 600-800 °C with a maximum at 700 °C; this exothermic peak is presumed to be associated with the crystallization of the spinel NFO.
The presence of only a single exothermic event for the amorphous→spinel conversion, indicates that the NFO spinel crystallization is a one-step process and no intermediate transformation occurs between the amorphous and crystalline phase.

4.3.2 Si/NFO Thin Films Processing Parameters

To study the effect of the processing conditions on the microstructure and properties of the NFO thin films on Si (100) substrates, the deposition parameters, including pyrolysis temperature, annealing temperature and annealing time, are varied according to Table 4-1.
Table 4-1 Studied processing conditions to grow the Si/NFO thin films.

<table>
<thead>
<tr>
<th>Pyrolysis T (°C)</th>
<th>Annealing T (°C)</th>
<th>Annealing time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>650</td>
<td>10</td>
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<tr>
<td>200</td>
<td>700</td>
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<td>-</td>
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</table>

*Effect of the Pyrolysis Temperature*

The Si/NFO thin films are prepared via spin coating the 0.5M solution onto the Si substrates. To study the effect of the pyrolysis temperature, the films are pyrolyzed (dried) for one minute on a hotplate at temperature ranging from 100 °C to 500 °C. All of the films are then rapid thermally annealed at 750 °C for 10 min. The θ-2θ XRD patterns of the 110 nm-thick films pyrolyzed at different temperatures are shown in Figure 4-2.
For all pyrolysis temperatures, the cubic spinel NFO phase is detected without any detectable secondary phases. The spinel phase shows random orientation closely matching the powder diffraction of nickel ferrite (ICDD PDF card No. 10-0325). From the XRD results, no difference in crystallinity between the samples is seen and all of the samples have similar XRD patterns.

Similar crystallinity can also be confirmed from top view SEM images shown in Figure 4-3. All of the films have comparable grain morphology with grain size of about 40 nm.
Figure 4-3 Top view SEM micrographs of the Si/NFO thin films pyrolyzed at various temperatures ranging from 100 °C to 500 °C. All films are annealed at 750 °C for 10 min.

Cross sectional SEM images of the Si/NFO films pyrolyzed at 100 °C and 500 °C are compared in Figure 4-4. These images also do not show significant difference in shape and size of the grains, indicating no effect of pyrolysis temperature on the crystal structure and grain size of the grown films.
In thin film fabrication by chemical solution processing, the solvent begins to dry during the coating process. The amorphous film forms during the drying (pyrolysis) step while the organic species decompose. In the NFO solution this temperature is 350 °C, below which the TGA curve shows weight loss and the DTA curve shows two peaks most likely associated with solvent evaporation and precursor decomposition.

At this stage the amorphous clusters form before complete elimination of the organic materials, which act as a nucleation barrier. At higher temperature annealing, densification and crystallization of the film begins and leads to a crystalline thin film. Since the pyrolyzed film is amorphous, the crystallization occurs by nucleation and growth during high temperature annealing.

Figure 4-5 shows a schematic diagram of the relative free energies of a crystalline film and an amorphous, sol-gel-derived layer.
Figure 4-5 Schematic diagram of the free energies of a sol-gel derived amorphous film and the crystalline phase.

From Figure 4-5, it can be concluded that the crystallization transformation in an amorphous phase is driven by the large free energy difference. This energy difference defines the energy barrier of both heterogeneous (at the interface and the free surface) and homogenous (through the bulk) nucleation and it can be overcome during the heat treatment.

The characteristic of the nucleation and growth during the annealing step define the resulting films’ microstructure. In the Si/NFO thin films, during annealing the homogenous nucleation throughout the film as well as the interface-nucleation of the randomly oriented grains leads
to a polycrystalline structure with equiaxed grains and the pyrolysis step does not affect the films’ microstructure 3.

Despite the similar uniform grain shape and size in all of the samples, less than 6% localized porosity is observed in the film pyrolyzed at 100 °C. The porosity can be caused by incomplete solvent evaporation during pyrolysis and boiling off the remaining solvent compounds during annealing.

The magnetization properties of the films pyrolyzed at different temperatures also exhibit very similar behavior with comparable magnetization saturation (200 kA/m), coercivity (15.9 kA/m) and remanence values (33 kA/m) (Figure 4-6). Similarity in magnetic behavior is a result of analogous microstructure.
Based on the DTA/TGA results, and knowing that varying the pyrolysis temperature doesn’t affect the films’ microstructure and the magnetic properties, 400 °C is chosen as the pyrolysis temperature for remaining sample preparation. TGA data shows that 400 °C is above the solvent evaporation and precursor decomposition temperatures, and that no weight loss occurs above that temperature.

**Effect of the Annealing Temperature**

To study the effect of the annealing temperature on the microstructure and properties of the Si/NFO thin films, annealing temperatures are varied based on the DTA.
The films are deposited onto the Si substrate with the same spin coating procedure (2000 rpm × 30 sec), resulting in a final film thickness of 110 nm. The films are pyrolyzed at 400 °C for one minute and then annealed at various annealing temperatures from 650 °C to 900 °C for 10 min according to Table 4-1.

The θ-2θ XRD results for the NFO thin films annealed at various temperatures are illustrated in Figure 4-7. In all samples, peaks related to the NFO spinel cubic structure are observed and no preferred orientation is seen. At an annealing temperature of 650 °C, the film is either not well crystallized or the grain size is particularly small, as evidenced by wide, weak peaks. With increasing annealing temperature, the spinel NFO peaks sharpen and their intensity increases, indicating more complete crystallization in the sample.
Figure 4-7 XRD patterns of 110 nm-thick Si/NFO thin films annealed at various temperature from 650 °C to 900 °C for 10 min. Before annealing, the films are pyrolyzed at 400 °C for one minute.

Top view SEM images of the Si/NFO thin films annealed at various temperatures are displayed in Figures 4-8 and 4-9. The film annealed at 650 °C shows homogenous grain nucleation with an average grain size of 25 nm, which is consistent with the observation of wide, shallow peaks in the XRD patterns. The average grain size increases to 55-60 nm for the film annealed at 900 °C, consistent with sharper peaks in the XRD patterns.
For all temperatures, finer grain structure is observed close to the substrate. The finer grain size in proximity to the substrate can be caused by moving the pre-existing amorphous
clusters toward the substrate driven by solvent evaporation during spin coating and/or pyrolysis. Moreover, during annealing, a large in-plane stress caused by the thermal expansion mismatch between the film and the substrate results in extensive nucleation adjacent to the substrate surface \(^1\).

Effects of the annealing temperature on the room temperature magnetization behavior of the Si/NFO films are also studied. The results are shown in Figure 4-10. The saturation magnetization (\(M_s\)) increases with annealing temperature. The film annealed at 900 °C has the highest \(M_s\), which is above the reported value of the bulk NFO (270 emu/cm\(^3\), indicated with a dashed line) at 300 K \(^4-6\). Similar to previous reports for CoFe\(_2\)O\(_4\) thin films, increased annealing temperature and consequently grain size increases \(M_s\) \(^7\). However, the observed increase in the saturation magnetization with increased grain size is converse to the dependence of the magnitude of \(M_s\) on the material chemistry rather than the microstructure \(^8\). For ferro/ferrimagnetic materials, the microstructure affects the shape of the M-H curve (coercivity and remanent magnetization) and the strength of the field at which the saturation magnetization is attained \(^8,9\).
Figure 4-10 Magnetization hysteresis loops of the Si/NFO films annealed at temperatures ranging from 650 °C to 900 °C.

To investigate the possible contribution of a magnetic secondary phase which might not be detected in XRDs, electron diffraction study is performed on the samples annealed at 700 °C, 800 °C and 900 °C. Figure 4-11 shows the selected area electron diffraction (SAED) patterns and the corresponding bright field contrast TEM images.
Figure 4-11 Plan-view bright field TEM images and corresponding electron diffraction patterns of the Si/NFO thin films annealed at 700 °C, 800 °C and 900 °C.
The TEM images show the increased grain size with increased annealing temperatures. The SAED patterns confirm the purity of the nickel ferrite and absence of any secondary phases. Therefore, the higher Ms of the Si/NFO annealed at 900 °C could not be related to any magnetic impurity or secondary phase.

The observed increase in saturation magnetization with increased grain size (Figure 4-10) may be explained by changes in the cation distribution (i.e. cation disorder), which can be affected by the synthesis conditions and/or the strain the film. The magnetic properties of spinel oxides are governed not only by the type of cation in the lattice, but also by their distribution over the available crystal sites \(^{10}\). The dominant magnetic exchange coupling which define the net magnetic behavior of the spinel ferrite is between the cations positioned in the octahedral and tetrahedral sites. In an ferrimagnetic ferrite with an inverse spinel structure such as NFO, the Fe\(^{3+}\) ions are distributed evenly between the octahedral and tetrahedral sites and the other cations are located in the octahedral sites \(^{8}\). In spinels the dominant magnetic interaction is an exchange coupling between cations in the octahedral and tetrahedral sites. In NFO, the magnetic moment per unit chemical formula is equal to that of the Ni\(^{2+}\) ion, since the Fe\(^{3+}\) ions have antiferromagnetic coupling through an indirect exchange interaction \(^{6}\). Hence, only slight changes in the cation distribution could interrupt the antiferromagnetic exchange coupling between the Fe\(^{3+}\) ions, increasing the magnetic properties. This may play a major role in observing the higher Ms for the Si/NFO films annealed at 900 °C than the Ms value of the bulk sample.
For the lowest annealing temperature (650 °C), the remarkably low magnetization results from the high density of amorphous regions due to incomplete crystallization and very small grain size (large grain boundary density). The higher grain boundary density in lower temperature-annealed samples may also be responsible for the lower magnetic properties.

The effect of the annealing temperature on the Si/NFO thin films’ coercivity is displayed in Figure 4-12. As the grain size increases with increased annealing temperature, the coercive field increases, plateauing at about 200 kA/4πm for annealing at and above 750 °C. By decreasing the density of grain boundaries (increasing the grain size) in polycrystalline materials, the volume fraction of amorphous regions decreases, increasing the magnetization; the magnetic interaction tends to be weaker in a disordered phase. The effect of grain size on magnetic properties has been extensively studied on nanocrystalline materials where the exchange coupling between grains reduces the magnetic anisotropy and coercivity\textsuperscript{9,11}.
To minimize the interfacial diffusion between the NFO and substrate, as well as the piezoelectric phase (e.g. PZT) in the magnetoelectric composites, the lowest crystallization temperature (750 °C) in which the film is fully crystallized is chosen as the annealing temperature for subsequent sample preparation.

**Effect of the Annealing Time**

To study the effect of the annealing time on the film crystallinity, the XRD patterns are collected from the Si/NFO thin films annealed for 1, 10 and 30 minutes at 750 °C, a temperature at which the film is well crystallized (Figure 4-13). The results indicate that an
annealing time of 1 minute is insufficient to fully crystallize the films. After 10 and 30 minutes, the NFO inverse spinel structure is observed with neither a preferred orientation nor any secondary phase peaks; little difference is seen between the films annealed for 10 and 30 minutes.

Figure 4-13 XRD patterns of the 110 nm-thick Si/NFO thin films annealed at 750 °C for 1, 10 and 30 min.
The effect of the annealing time at 750 °C on the magnetic behavior of the NFO thin films is also studied in Figure 4-14; the M-H curves for the samples annealed for 10 and 30 min show similar behavior and comparable $M_s$ values: both samples, however, exhibit higher magnetization value compared to the sample annealed for one minute, indicative of increased grain size and decreased grain boundary density. As observed in the XRD results, an annealing time of 1 minute is insufficient to fully crystallize the film and results in higher density of amorphous regions. Since the magnetic interaction tends to be weaker in an amorphous phase, the film shows lower magnetic properties.
The thin film thickness is an important parameter for many applications, and in some situations a large film thickness is needed. To increase the film thickness, and to study the effect of an additional annealing cycles on the film microstructure, a second layer of NFO film is deposited atop the previous layer to reach the desired thickness. Each layer is pyrolyzed and annealed individually.
Figure 4-15 shows a cross-sectional HIM image of the two-layer NFO thin film on a Si substrate. Each layer has been pyrolyzed at 400 °C and annealed at 750 °C for 10 min. A homogenous microstructure with an average grain size of about 40 nm is observed. There is no evidence of change in microstructure and grain size in the second layer. Hence, it can be concluded that the proposed chemical route has the ability to be repeated for multiple layers to achieve the desired thickness without changing the microstructure of the films.

Figure 4-15 Two layers of the NFO deposited on the Si substrate, pyrolyzed at 400 °C and annealed at 750 °C for 10 min.
Atomic Force Microscopy (AFM)

Topographic atomic force microscopy (AFM) images of the NFO thin films grown on Si substrates and heat treated in 750 °C for 10 min are displayed in Figure 4-16. The AFM images confirm the granular microstructure of the film. The surface roughness (rms) is determined to be 3.5 nm.

Magnetic Force Microscopy (MFM)

When the surface of the Si/NFO (pyrolyzed at 400 °C and annealed at 750 °C for 10 minutes) is scanned with a magnetic cantilever (MFM), as shown in Figure 4-17, magnetic domains,
observed as regions of light and dark contrast with an average size of 150 nm. The domain pattern is irregularly spotted and the randomness in the magnetic domain structure confirms the random orientation and presence of no magnetic anisotropy in the film. The observed domain structure on the polycrystalline NFO surface is complex, since the grain boundaries act as a barrier to interrupt the continuity of magnetization from one grain to another one. Hence, because the magnetic easy axis is different for two adjacent grains, the grains boundaries are also the magnetic domain boundaries which act as obstacle during magnetization.

![Figure 4-17 MFM top view scan of the Si/NFO thin film.](image)
Transmission Electron Microscopy (TEM)

To study the form and size of the NFO grains and any possible interdiffusion between the NFO film and Si substrate, the films annealed at 750 °C for 10 min have been examined by TEM. The images are illustrated in Figures 4-18 to 4-21.

The polycrystalline NFO grain structure is evident in the bright field TEM image taken from the cross-section of a 110 nm thick film. The grains have irregular shapes with sizes varying from 40 nm to 50 nm. At higher magnification, well-crystallized NFO grains are evident and no change of crystal structure is observed at the interface with the substrate. The NFO grains are grown on a native oxide layer (amorphous SiO$_2$) and there is no sign of formation of secondary phases at the interface, which is also confirmed by the SAED pattern (Figure 4-10). Intergranular porosity is observed, however, in some images (Figure 4-19). Such porosity is undesirable as it will decrease the volume fraction of the magnetic material as well as impede domain wall motion.
Figure 4-18 Cross-sectional TEM images of the Si/NFO films annealed at 750 °C for 10 min.

Figure 4-19 An intergranular porosity in the NFO thin film.
Top view TEM micrographs of the NFO thin film and the corresponding electron diffraction pattern (Figure 4-20) confirm that the NFO is randomly oriented. No segregation or secondary phases is observed in the TEM images or distinguished in the electron diffraction pattern.

Figure 4-20 Top view TEM images of the NFO thin films on silicon substrate and the corresponding electron diffraction pattern.
4.4 Summary

A new 2-MOE (CH₃OCH₂CH₂OH) solvent-based chemical route is developed to deposit NiFe₂O₄ (NFO) thin films. Randomly oriented pure NFO thin films by inverse spinel structure are deposited onto Si (100) substrates using the proposed chemical solution process. The effect of processing conditions, including the pyrolysis temperature and the annealing time and temperature, are studied on the deposited NFO thin films. The microstructural studies and magnetic properties measurements show that changes in the pyrolysis temperature do not affect the film morphology and the magnetic properties. The 400 °C pyrolysis temperature is chosen for consequent sample preparation because it is above the solvent evaporation and precursor decomposition temperatures.

It is shown that the heat treatment conditions define the microstructure and the film morphology and consequently the magnetic properties. Based on the microstructural and magnetic studies, the chosen annealing conditions to deposit the NFO thin film on Si substrate is heat treatment at 750 °C for 10 min.

The TEM microstructural studies exhibit neither any interdiffusion between the film and substrate nor any secondary phase in the NFO films.

4.5 References


5.1 Motivations

An alternative approach to overcome the small magnetoelectric (ME) coupling in single phase materials such as Cr$_2$O$_3$ \(^1\) is presented by heterogeneous composites. In these composites, the strain coupling at the interface between the piezoelectric and magnetostrictive phases results in ME behavior\(^2-6\). NiFe$_2$O$_4$ (NFO) as a one of the most important ferrites, has shown efficient mechanical bonding to Pb[Zr$_x$Ti$_{1-x}$]O$_3$ (PZT), one of the most widely used piezoelectric materials, in bilayered ME composites \(^3,4,6-13\). NFO does not react with PZT, even at temperatures as high as 1050 °C,\(^14\) and as a result, NFO/PZT laminated composites have shown moderate magnetoelectric behavior\(^15\).

No systematic investigations on the properties of thin film NFO/PZT multilayered composites have been reported, nor have microstructural studies of thin- or thick-film NFO/PZT multilayers. Nor are there reports on the NFO interface with the piezoelectric phase. In addition, despite a large number of studies on laminated thin film multiferroic composites, there is a lack of research on elemental interdiffusion between layers. In this chapter, the fabrication of NFO/PZT laminated thin film composites via chemical solution deposition is reported. The magnetic and ferroelectric characterizations of the prepared composites are studied as well as the microstructures of the deposited films in the film bulk
and at the interface. The interface is engineered to minimize the elemental interdiffusion between phases.

5.2 Approach

5.2.1 Sample Preparation

Multilayered thin film composites are prepared by spin coating the NFO and PZT precursor solutions onto substrates as described in chapter 2. Spinning speeds of 3000 rpm and 2000 rpm (for 30 sec) are used for the NFO and PZT, respectively. Each PZT layer is pyrolyzed at 375 °C for 1 minute to remove the solvents and create an amorphous film, before rapid thermal annealing at 650 °C for 1 minute to crystallize the perovskite phase. Each NFO layer is pyrolyzed at 400 °C for 1 minute and then annealed at 750 °C for 10 minutes (optimized condition from chapter 4). Pyrolysis and annealing are performed in air for both materials.

Two geometries of laminated composites are prepared (Figure 5-1). In both composite geometries, eight layers of PZT (475 nm in total) and three layers of NFO (310 nm in total) are deposited. Each layer is pyrolyzed and annealed. In the Si/NFO/PZT configuration (type I), the PZT layers are deposited directly onto NFO, whereas in the Si/NFO/Pt/PZT configuration (type II), a thin layer of Pt (90 nm) is sputter deposited onto the NFO layer before PZT deposition. This allows comparison of the PZT layer formed on NFO with that formed on Pt, and a determination of the effectiveness of NFO as an electrode for charge extraction in magnetoelectric applications. For all configurations, circular Pt top electrodes
(70 to 520 μm in diameter) are sputtered atop the PZT layer using a patterned sputtering mask.

Figure 5-1-Schematic drawings of the heterogeneous multilayer composite geometries (not to scale) (type I) Si/NFO/PZT and (type II) Si/NFO/Pt/PZT.

5.2.2 Characterization and Tests
The phase and crystallographic orientation of the deposited films are characterized by θ-2θ X-Ray diffraction (XRD) with Cu Kα radiation (λ=1.5418Å). The cross-sections of the samples are examined by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM). The elemental depth profiles are analyzed by secondary ion mass spectroscopy (SIMS). To study the surface morphology of the grown ferrite films, atomic force microscopy (AFM) is performed. The ferroelectricity and magnetization of the composites are also evaluated.
5.3 Results and Discussion

5.3.1 Characterization

The XRD results of both composite configurations are shown in Figure 5-2. Pure perovskite PZT is successfully grown on NFO and NFO/Pt; no peaks associated with secondary phases are observed in both configurations. The PZT films grown onto NFO/Pt (type II) show improved crystallinity as compared to the PZT grown directly on the NFO (type I), as evidenced by increased intensity of the perovskite-related peaks.

Figure 5-2 XRD patterns of the PZT/NFO multilayered type I and II composites.
It is important to consider the quantitative differences between the PZT peaks in the XRD patterns in the Figure 5-2. In a randomly oriented sample, the intensity of the PZT(100) peak relative to PZT(110) peak is 12% \^{16}. Here, in type I and type II composites, this ratio is increased to $\sim$28% and $\sim$60%, respectively. Thus, while the PZT films are not highly textured, in both configurations, they are partially $<100>$-oriented (fiber texturing) and the degree of orientation is higher in the films grown on an intermediate Pt layer.

For comparison, XRD patterns of the PZT grown on platinized silicon substrate (Si/SiO$_2$/TiO$_x$/Pt) and PZT grown on the Si/NFO are shown in the Figure 5-3. The PZT on Pt has a high degree of texture in $<100>$ direction, while on NFO, it is almost randomly oriented.

Figure 5-3 PZT grown on platinized Si and Si/NFO substrates.
The difference between the orientations of the grown PZT in type I and type II composites can be related to the roughness of the NFO surface seen in the AFM images. The NFO rms value of 3.5 nm favors randomly oriented PZT growth in NFO/PZT multilayers. For the NFO/Pt/PZT multilayer, the addition of sputtered Pt reduces the roughness of the surface (rms of 1.5 nm) upon which the PZT is deposited which may further enhance PZT growth in the (100) orientation. Alternatively, the enhanced (100) growth on Pt may be chemically induced texturing. Surface topography images of NFO and NFO/Pt are shown in the Figure 5-4.
Figure 5-4 AFM study of top surface of (a) Si/NFO and (b) Si/NFO/Pt.

Figure 5-5 displays cross-sectional backscattered-electron SEM micrographs of the type I and II multilayers. A clean interface between the PZT and NFO layers is clearly distinguishable in both images. The measured thicknesses of the NFO and PZT layers are 310 nm and 470 nm, respectively. In both films, PZT has a dense, columnar structure, whereas the NFO layer shows a fine grain structure with less than 1% porosity (based on digital image analysis), similar structure of single phase NFO thin film (Figure 5-13). Thus, the PZT synthesis process does not affect the NFO microstructure. Two contributing factors
to the microstructural difference between the PZT and NFO may be the difference in crystallization driving force for the PZT versus the NFO transformation and the different transformation pathway displayed by these materials.

Furthermore, the PZT in the type I composite appears less dense and with finer grains (60 nm in width) in comparison with that in the type II (110 nm in width). The difference between the grain size in both configurations also can be explained by the surface roughness which facilitates the nucleation of the PZT phase.

Figure 5-5 SEM micrographs of the (a) type I and (b) type II laminated composites.
Pores at the PZT layer are observed at higher thicknesses; indicated in Figure 5-6. Intergarnular porosity may be result of insufficient densification caused by rapid crystallization.

Figure 5-6 SEM micrograph of type II composite showing the porosity formed in the PZT layer. The arrows point to the intergranular porosity formed between PZT column.

The cross section of the type I composite is also examined by TEM (Figure 5-7). At low magnification, a relatively smooth NFO/PZT interface and dense, columnar growth of the PZT layer are evident. At higher magnifications, the NFO/PZT interface appears smooth with
no intermediate or transition region and hence strong coupling between the two phases is expected.

Figure 5-7 PZT/NFO interface of the type I multilayer composite at different magnifications.
The finer grain size in the NFO layer is observed in proximity to the substrate, which as explained in chapter 4 can be caused by clusters driven toward the substrate by solvent evaporation during the pyrolysis step.

There are also some interdiffusional regions in the substrate which are displayed at higher magnification in the Figure 5-8.

Figure 5-8 EDS analysis is performed by STEM from the diffusion regions in the Si substrate.
An EDS analysis (Figure 5-8) of the region of the Si/NFO interface shows some Pb and Fe diffusion through the substrate. Thus, the NFO layer, even with a 300 nm thickness, is not an effective barrier to Pb diffusion. It is important to note that Pb depletion by diffusion through NFO to the substrate does not adversely affect the PZT phase purity, most probably due to the excess Pb in the initial precursor solution.

The Pb diffusion from the PZT layer through the NFO layer and to the Si substrate in the Si/NFO/PZT multilayer is confirmed via SIMS analysis as shown in Figure 5-9. In fact, the diffusion of Pb, as well as Zr and Ti, is evident in the chemical depth profiles. The Pb concentration is much higher than the other elements and is highest at the NFO/Si interface. Within the NFO layer, Pb has segregated primarily between the (three) deposited NFO layers. In the type II multilayer, Pb diffusion decreases significantly and Zr and Ti diffusion is negligible (Figures 5-9 and 5-10), indicating that the Pt layer provides a partial diffusion barrier. Note that continuous Zr/Ti gradients (the concentration oscillation) within the PZT sub-layers, corresponding to each crystallized layer, have been previously reported and are attributed to the lower crystallization temperature for PbTiO$_3$–rich compositions relative to PbZrO$_3$-rich compositions in PZT solid solutions $^{17,18}$. 
Figure 5-9 SIMS analyses of the type I and type II composite configurations.
The Pb diffusion profiles in both composite configurations are compared in Figure 5-10.

![Figure 5-10 Pb diffusion comparison between type I and II configurations.](image)

### 5.3.2 Properties measurement

**Electrical polarization**

The dielectric polarization (P) versus electrical field (E) hysteresis at room temperature for the type I and type II composites are studied (Figure 5-11). Significant leakage current prevents direct confirmation of the ferroelectric behavior of the PE phase in the type I multilayer. Considering the absence of secondary phases or interfacial layers in this composite, however, the leakage is partially can be due to the use of the NFO layer as the bottom electrode as well as the Pb interdiffusion from the PZT layer to the NFO layer and the substrate. In comparison, the type II multilayer exhibits well-defined ferroelectric hysteresis
the dielectric losses are small and the remnant polarization \( (P_r) \), saturation polarization \( (P_s) \) and coercive electric field \( (E_c) \) are 22 \( \mu \text{C/cm}^2 \), 67.5 \( \mu \text{C/cm}^2 \) and 41 kV/cm, respectively. These values are comparable to those reported for sol-gel derived PZT films of similar composition and thickness\(^{19}\).

\[ \text{Figure 5-11- Electrical polarization hysteresis loops of type I and II composites.} \]

**Magnetization**

The room temperature magnetization curves of Si/NFO, type I and II composites show well-defined hysteresis with similar shapes (Figure 5-12). Relative to the Si/NFO films, the \( H_c \) values of type I and type II are 140% and 70% lower, respectively, while the \( M_s \) values are increased.
Figure 5-122 Magnetization hysteresis loops for pure NFO film, type I and type II composites.

The results are summarized in Table 5-1. The lower coercivity of the heterogeneous multilayers relative to the NFO film may be due to induced strain in the NFO film by the subsequently deposited PZT (and eventual Pt); this is in agreement with previously reported results on layered structures.\textsuperscript{20-23} PZT and NFO have significantly different coefficients of thermal expansion, $2\times10^{-6}$ K$^{-1}$ for PZT and $10^{-5}$ K$^{-1}$ for NFO \textsuperscript{23}, resulting in tensile strain in the NFO layer within the Si/NFO/PZT composite after cooling down from processing the PZT. It has been previously reported for other thin film ferrite/PZT multilayers that such biaxial tensile strains can induce significant magnetic anisotropy, reducing $H_c$ by up to 60%
In the Si/NFO/Pt/PZT multilayer, some of the effects of differential thermal contraction are mitigated because the coefficient of thermal expansion of Pt (8.8×10⁻⁶ K⁻¹) is close to that of NFO, and because metallic Pt has lower elastic modulus than NFO and PZT, particularly at the elevated processing temperatures. Thus, in the Si/NFO/Pt/PZT configuration the reduction in $H_c$ is only 40%.

Table 5-1 Magnetic behavior of the multilayer films

<table>
<thead>
<tr>
<th></th>
<th>Si/NFO (Si/NFO/PZT)</th>
<th>Type I (Si/NFO/Pt/PZT)</th>
<th>Type II (Si/NFO/Pt/PZT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_s$ (Oe)</td>
<td>2.2×10⁻³</td>
<td>2.6×10⁻³</td>
<td>2.8×10⁻³</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>208</td>
<td>88</td>
<td>122</td>
</tr>
</tbody>
</table>

Although previous reports indicate that a diamagnetic layer such as PZT can decrease the $M_s$ of the magnetic layer⁴,⁷,²⁴, here the addition of the PZT layer increases $M_s$ by at least 20%. This may be related to the PZT heat treatment. Since there are eight layers of PZT deposited, the NFO experiences an additional 8 minutes of annealing at 650 °C. Considering the effect of sintering time on the Si/NFO samples discussed in chapter 4, an increase in $M_s$ is not unexpected. The higher $M_s$ in type II as compared to type I may be due to the reduced Pb diffusion and the elimination of Ti and Zr diffusion shown in Figure 5-9. The presence of these impurities may reduce $M_s$, so the presence of the Pt layer indirectly increases $M_s$ by serving as a diffusion barrier.
5.4 Summary

Sol-gel derived NiFe$_2$O$_4$/Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (NFO/PZT) thin film multilayer composites, with and without an intermediate layer of platinum, are grown on silicon substrates. The fabricated configurations are Si/NFO/PZT (type I) and Si/NFO/Pt/PZT (type II) with 310 nm thickness of NFO, 475 nm thickness of PZT and 90 nm thickness of Pt. X-ray diffraction and scanning electron microscopy show formation of phase-pure spinel cubic NFO and tetragonal perovskite PZT in both configurations with no detectable intermediate/secondary phase.

Transmission electron microscopy (TEM) reveals a sharp interface between the NFO and PZT layers in type I multilayers. The presence of an intermediate Pt layer between the NFO and PZT significantly reduces Pb diffusion into the NFO and silicon substrate, as evidenced by TEM and secondary ion mass spectroscopy (SIMS). SIMS studies show NFO layer cannot act as a barrier to prohibit the elemental diffusion (Pb, Ti and Zr) from the PZT layer to the substrate. However, adding a 90 nm-thick layer of metallic Pt reduces the diffusion remarkably.

The magnetic properties of both composites are compared to the NFO thin films on Si substrates of the same thickness. The saturation magnetization of type I and type II multilayers increase by 20% and 25%, respectively, relative to the Si/NFO films. Both composites, however, show significant decrease in coercivity ($H_c$) compared to the Si/NFO thin films which can be explained by the strain in the film induced by thermal expansion/lattice misfit.
The intermediate Pt layer in the type II multilayer also reduces the leakage current compared to type I. The saturation polarization ($P_s$) and coercive electric field ($E_c$) of the type II multilayer are comparable to those reported for sol-gel derived PZT films of similar composition and thickness.

The type II multilayer has increased $M_s$, and $P_s$ along with reduced electrical leakage, in comparison to type I, and is thus a promising architecture for magnetoelectric behavior. The ME mechanical coupling, however, may be affected by the Pt stress-strain behavior. These effects may be mitigated by the relatively small Pt layer thickness that can be optimized further, as well as optimization of the relative thicknesses of the ME and PE layers.

5.5 References


CHAPTER 6

UNIAXIALLY TEXTURED NiFe$_2$O$_4$ THIN FILMS ON Si/SiO$_2$/TiO$_x$/Pt(111) SUBSTRATES

6.1 Motivation

Although thin films are an advantageous geometry for device applications, few studies on oriented NFO thin films have been reported, and the only studies on epitaxial or textured films involve films prepared by pulsed laser deposition $^{1-4}$, DC sputtering $^{5,6}$ or chemical vapor deposition $^7$ techniques. These processing techniques tend to be more complex and more expensive than chemical solution deposition (CSD) approaches. To date, the only published study on easy-axis textured ferrite films via CSD reports on M-type hexagonal barium ferrite grown by metallo-organic decomposition $^8$. In this work, the barium ferrite films (230 nm thick) grown on Pt templates have a Lotgering factor of 95.3% in the c-axis direction and an out-of-plane remanence ratio ($M_r/M_s$) of 93% $^8$. In comparison to barium ferrite, NiFe$_2$O$_4$ (NFO) is a soft magnetic spinel ferrite with higher permeability and lower eddy current losses, making it preferable for high frequency (1-100 GHz) applications $^9$. Studies of CSD processed spinel cubic ferrite thin films, such as CoFe$_2$O$_4$ and NiFe$_2$O$_4$, have resulted only in randomly oriented polycrystals $^{10-16}$.

In this chapter the fabrication of highly textured polycrystalline NFO thin films on platinized silicon substrates (Si/SiO$_2$/TiO$_x$/Pt (111)) via CSD is discussed. The resulting films show a
strong degree of preferential growth in the $<111>$ direction, the NFO easy-axis direction, and enhanced magnetic properties.

6.2 Approach

NFO thin films are synthesized by spin coating ($2000 \text{ rpm} \times 30 \text{ sec}$) a 0.5 M NFO precursor solution onto Si/SiO$_2$/TiO$_x$/Pt (111) substrates. The (111) polycrystalline platinized silicon wafers are supplied commercially by MEMS and Nanotechnology Exchange. After deposition, the films are pyrolyzed at 400 °C for 1 minute to remove the solvent, decompose the precursors, and form an amorphous layer. The films are subsequently annealed (750 °C for 10 min) to crystallize the NFO spinel phase, resulting in 110 nm-thick films. For comparison, NFO films are also grown onto Si/SiO$_2$ substrates (Si-NFO) using similar deposition and annealing conditions. To study the effects of the film thickness on crystallographic structure and magnetic properties of the films, uniaxially textured NFO films on platinized Si substrates (Pt-NFO) are prepared with thicknesses ranging from 50 nm to 140 nm by varying the spin coating speed. Film thicknesses are measured by cross-sectional scanning electron microscopy (SEM).

6.3 Results and Discussion

6.3.1 Characterization

XRD patterns of 110 nm-thick films in Figure 6-1 show inverse spinel cubic NFO in both Si-NFO and Pt-NFO films with no detectable secondary phases. The XRD profile for a
platinized silicon substrate is also shown as a reference. The Si-NFO film is randomly oriented, with an XRD pattern closely matching powder diffraction of NFO (ICDD PDF card No. 10-0325) with the strongest peak corresponding to the <311> diffraction at 35.7° (as discussed in chapter 4). Conversely, the XRD pattern of the Pt-NFO film shows a strong degree of preferential growth in the <111> direction. The degree of <111> preferential growth in the 110 nm-thick Pt-NFO film, estimated using Lotgering’s orientation factor 17, is ~90%. The Pt-NFO films also show high intensity peaks corresponding to the spinel structure, which are not as visible in the Si-NFO films, indicating enhanced crystallinity in the textured films.
Figure 6-1 X-ray diffraction patterns of randomly oriented and (111) textured 110 nm-thick NFO films deposited on Si and Si/SiO$_2$/TiO$_x$/Pt substrates. The XRD pattern of the Pt substrate is also shown for comparison.

Top view SEM micrographs in Figure 6-2, however, do not show clear differences in grain morphology, and both films have an average grain size of about 40 nm. The cross-sectional SEM micrographs of the cleaved thin film samples confirm polycrystalline NFO films with similar microstructures on both substrates.
The degree of $<111>$ alignment in the Pt-NFO thin films is examined via X-ray pole-figure analysis around the [222] NFO direction (Figure 6-3). For the Si-NFO films, the low pole density in the large range of tilt angle ($\chi$) up to 89° confirms a randomly oriented polycrystalline film. For the Pt-NFO films, however, the sharp diffraction intensity concentrated at the center of pole figure ($\chi=0\pm6^\circ$) illustrates strong $<111>$ texture in out-of-plane direction of the films. Thus, in the Pt-NFO films, the magnetic easy-axis is normal to
the film plane. The <440> diffractions, found at a 35.2° inclination in χ, confirm the preferred orientation of the (111) planes normal to the sample surface but the uniform intensity along 360° in φ indicates random in-plane orientation.

Figure 6-3 X-ray pole figures of (a) randomly oriented Si-NFO and (b,c) (111) textured Pt-NFO films. The fixed 2θ angles are associated with (222) (Fig. (a) and (b)) and (440) (Fig. (c)) peaks. All films are 110 nm-thick.

6.3.2 Effect of Film Thickness on Degree of Texture

The effect of NFO thickness on the crystallographic texture in the Pt-NFO thin films, for thicknesses ranging from 50 nm to 150 nm, is illustrated in Figure 6-4. In all films, preferred growth in the <111> direction is observed. The highest degree of texture is achieved in the thinnest film (50 nm) and the intensity of peaks associated with other crystallographic orientations (i.e., (220), (422), (400) and (440)) increases with increasing film thickness. As seen in the Figure 6-1 and the inset of the Figure 6-4, the (311)
NFO and $K_\beta$ (111) Pt partially overlap, so the presence of an intense peak at 35.9 ° in the thinner films is likely due to the substrate.

Figure 6-4 X-ray diffraction patterns of the (111) textured NFO films on Si/SiO$_2$/TiO$_x$/Pt substrates as a function of NFO thickness. Inset shows the overlap of (311)NFO and $K_\beta$ (111)Pt peaks. 

(111)Pt peaks.
The effect of film thickness on orientation in the PbTiO$_3$ thin films derived via sol-gel processing is also observed by Chen et al.$^{18}$ It is reported that as film thickness increases, the degree of orientation decreases.$^{18}$ The orientation dependence on film thickness can be explained by the model proposed by Schwartz et al.$^{19}$ Based on this model, effects of film thickness on the microstructure are expected due to the change in time required for the growth of the interface-nucleated grains to consume the amorphous layer. In general, three types of nucleation are probable in film crystallization from an amorphous layer; interface nucleation of oriented grains, bulk nucleation and surface nucleation (Figure 6-5). Typically, nucleation at the interface is the most energetically favorable nucleation event for films deposited on substrates with a reasonable degree of lattice matching.$^{19}$
In thicker films, the required time for growth of the interface-nucleated grains to reach the surface is higher than in thinner films. Hence, because a higher temperature is reached prior to the completion of the crystallization of initially nucleated grains at the interface, other nucleation events such as surface nucleation and bulk nucleation are possible, which decrease the total degree of texture of the film.¹⁹
6.3.3 Microstructural Studies

The top-view TEM images of the textured Pt-NFO thin films (Figure 6-6) illustrate that the oriented NFO grains have similar shape and size of about 40 nm as in the non-oriented Si-NFO films as shown in figure 4-17 of chapter 4.

The selected area electron diffraction (SAED) pattern of the textured Pt-NFO films (Figure 6-6d), however, confirms the grains are aligned along the <111> direction. The dark-field diffraction contrast image, corresponding to the (111) plane of the textured NFO films (Figure 6-6c), shows a high density of oriented grains.
Figure 6-6 Top view bright field images in two magnifications (a and b), dark field diffraction contrast image corresponding to (111) diffraction (c) and SAED pattern of the Pt-NFO films.
The cross-sectional TEM images of the Pt-NFO films are shown in Figure 6-7 in different magnifications.

![Figure 6-7 Cross-sectional bright field TEM images of the Pt-NFO thin films in different magnifications.](image)

The microstructure of the textured NFO is granular similar to the Si-NFO films, but more compact with less porosity across the film. The corresponding bright and dark field cross-sectional TEM image (Figure 6-8) show island nucleation and growth (Volmer-Weber mechanism)\(^{20}\) and each island follows the substrate grain structure.
Figure 6-8 bright (a) and dark (b) field cross-sectional images showing island growth mechanism for NFO grains in Pt-NFO thin films.

Beyond the first layer of grain nucleation and growth at the substrate interface, continuity across adjacent grains is not observed. In this region, the texture is not influenced by the substrate but instead by the processing parameters. Therefore, random grain nucleation is likely due to competitive homogeneous and heterogeneous nucleation activation energies.

The enhanced texture in the Pt-NFO is driven by NFO grain nucleation at the Pt surface, which is initiated by lattice matching between Pt and NFO. The d-spacings of Pt(110) and NFO(110) ($d_{Pt}$ and $d_{NFO}$) are 5.54 Å and 11.79 Å, respectively. Therefore, similar to what is observed in domain matching epitaxy, the small lattice mismatch by double lattice matching drives the nucleation of NFO grains with a preferred (111) orientation atop the
(111)-textured Pt substrate (Figure 6-8b). The resulting localized epitaxy subsequently governs the texture development in the layer in direct proximity to the Pt-NFO interface. The epitaxial nucleation is enhanced by the low interfacial energy of the (111) planes in the NFO film. The interfacial energy decreases with increasing atomic plane density at the film/substrate interface. According to the periodic bond chain model, the planes with the highest number of uninterrupted strongest bonds have the smallest energy and hence crystal growth in that direction is favored. In NFO, the (111) planes have the highest planar density and the lowest energy. Thus, (111) oriented growth is preferred.

After complete coverage of the substrate, texture is controlled by the surface energy of the plane, $\gamma_{(hkl)}$, and the grains with minimum $\gamma_{(hkl)}$ surfaces grow preferentially. As the film grows, the individual islands impinge upon adjacent grains. Due to the in-plane randomness of the Pt substrate, the NFO film does not show in-plane orientation and thus is uniaxially textured.

6.3.4 Magnetic Properties

The in-plane and out-of-plane magnetization hysteresis loops for the 50 nm-thick <111> textured NFO films are shown in Figure 6-9.

The presence of strong perpendicular magnetic anisotropy in the films is evidenced by the lower saturation magnetic field (i.e., the particularly square shape of the hysteresis loop) and the increased ratio of the magnetic remanence to the saturation magnetization ($M_r/M_s$ ratio) in the out-of-plane magnetization; this is expected based on the out-of-plane texturing of the
NFO film along the magnetic easy-axis. The out-of-plane magnetic response also exhibits large hysteresis with coercivity ($H_c$) close to $\sim 700$ Oe compared to the in-plane response with $H_c \sim 220$ Oe. Due to the shape anisotropy in thin films, the coercivity of the NFO films is amplified in the out-of-plane measurement. The shape anisotropy in thin films favors in-plane magnetic moment orientation in order to minimize the magnetostatic energy. For the $\langle 111 \rangle$ textured NFO films, however, the coercivity enhancement is larger than in the randomly oriented Si-NFO films of the same thickness, for which the in-plane and out-of-plane coercivities are $\sim 220$ Oe and $\sim 600$ Oe, respectively.

Figure 6-9 Room temperature in-plane and out-of-plane magnetization hysteresis loops for 50 nm-thick textured NFO thin films on Si/SiO$_2$/TiO$_x$/Pt substrates.
Figure 6-10 compares the room temperature out-of-plane magnetization curves for the textured Pt-NFO films of varying thickness from 50 nm to 150 nm. The magnetization for a 110 nm-thick randomly oriented NFO thin film on Si is shown also for comparison.

![M-H Curves](image)

Figure 6-10 Room temperature out-of-plane magnetization hysteresis curves for the random and textured NFO films of different thicknesses.

The M-H curves for the textured (Pt-NFO) films are more squarely shaped than the randomly oriented film (Si-NFO). With decreasing thickness and increased the degree of texture, the magnetization shifts to higher values and becomes increasingly square. The out-of-plane
M_{r}/M_{s} ratio improves from 30% in the 150 nm-thick textured NFO to ~73% in the 50 nm-thick films.

With the high degree of <111> texture normal to the film plane, a higher degree of magnetic anisotropy is expected than observed. A number of factors contribute to this imperfect behavior. In the thicker films, the presence of misaligned grains (bulk and surface-nucleated grains) plays a role in reducing the overall magnetic anisotropy. In the 50 nm-thick NFO film with nearly perfect (111) texture, however, the magnetization hysteresis is expected to be completely square or nearly so, and the deviation observed is greater than expected solely from the small departure from perfect texture. The small non-ideal magnetic behavior thus likely results from strain in the NFO lattice in the vicinity of the Pt substrate due to misfit and/or internal stress, induced during processing. The in-plane misfit strain is estimated by

\[ \varepsilon_x = \varepsilon_y = \frac{d_{NFO} - d_{Pt}}{d_{NFO}} = 6\%. \]

Due to the small, negative magnetocrystalline anisotropy (K_{1} \sim -0.62 \times 10^{-5} \text{ erg/m}^{3}), the stress anisotropy induced from the compressive strain in the NFO films dominates, particularly at low thicknesses. The influence of magnetostriction on the remanence ratio of polycrystalline materials is important in low anisotropy materials where the internal stress is sufficient to compete with K_{1}. Due to the unquenched orbital momentum of the A-sublattice Ni^{2+} ground state, NFO is highly stress-sensitive \(^{24}\). The small negative magnetostriction constant of NFO (\lambda_s =50 \text{ ppm}) indicates that the internal stress may be sufficient to compete with magnetocrystalline anisotropy (i.e. K_{1}<< \sigma \lambda_s) \(^{24}\).
In comparison to (111) textured/epitaxial NFO films fabricated by other techniques, the textured NFO films reported here show similar $M_r/M_s$ ratio at similar thicknesses. The $M_r/M_s$ ratio reported here for the 110 nm-thick films (55%) is comparable to that reported for an epitaxial 100 nm-thick NFO film sputtered onto a SrTiO$_3$ and Y$_{0.15}$Zr$_{0.85}$O$_2$ single crystal substrate and annealed at 800 °C (~60%) $^5$. The highest $M_r/M_s$ ratio reported for the NFO films, 80%, is achieved in a similarly sputtered film, also onto a SrTiO$_3$ and Y$_{0.15}$Zr$_{0.85}$O$_2$ single crystal substrate, and annealed at 1000 °C $^5$. This ratio is close to what is observed here in the 50 nm-thick films crystallized at 750 °C. In the case of the epitaxial NFO films grown by PLD, nearly-perfect square-shaped out-of-plane magnetization is reported for a 1400 nm-thick film on a MgO substrate, deposited at 900 °C and post-annealed at 1000 °C for 4 hours $^4$. Although the M-type barium hexagonal ferrite films (230 nm-thick) grown using CSD shows very high $M_r/M_s$ ratio, 93%, this high value is accomplished due to the high, positive anisotropy constant of this material ($K_1=3.4\times10^6$ erg/cc) compared to NFO, which mitigates the effects of mismatch and thermal stresses in the film as well as high thickness of the grown film.

The textured films grown here by CSD are deposited and annealed at much lower temperature than previously reported epitaxial/textured NFO films, yet the magnetic anisotropy is comparable. Thus, the proposed chemical solution route offers a cost-competitive processing method for the creation of textured magnetostrictive films on Si substrates. Additionally, the lack of epitaxial growth requirement and the lower processing
temperatures enables improved compatibility for co-processing of such films with piezoelectric layers for magnetoelectric composites.

6.4 Summary

Highly textured (111) NiFe₂O₄ thin films are prepared via chemical solution deposition onto Si/SiO₂/TiOₓ/Pt (111) substrates. Although the films show high degree of (111) texture in out-of-plane direction, they exhibit fully random orientation in the film plane.

With decreasing the NFO films’ thickness, nearly complete uniaxial texture is achieved. The TEM microstructural studies show that the textured growth is nucleated by lattice matching at the Pt/NFO interface which is also enhanced by the low surface energy of the (111) NFO planes. The magnetic properties of the textured films show improvements in remanent magnetization and coercivity relative to the randomly oriented films and are comparable to those grown by PLD and sputtering of the same thickness. However, with the high degree of <111> texture normal to the film plane, a higher degree of magnetic anisotropy (higher remanet ratio) is expected than observed. This small deviation from the perfect behavior can be contributed partly to the presence of misaligned grains (bulk and surface-nucleated grains) in the thicker films. In the thinner films, however it can mainly be explained by the strain in the NFO lattice in the vicinity of the Pt substrate due to thermal expansion/lattice misfit, which due to the small, negative magnetocrystalline anisotropy constant of the NFO (K₁ ∼ -0.62×10⁻⁵ erg/m³), can dominate the film magnetic anisotropy. To overcome the effect of the
film stain it is required to grow higher thickness of the NFO with higher/complete out-of-plane texture.

6.5 References


7.1 Motivation

For many applications, it is of interest to leverage the large magnetic anisotropy in magnetic thin films that results from texturing films in the energetically favored magnetic direction, the easy axis direction. Hence, controlled texturing of NFO thin films is crucial for tailoring properties and maintaining consistent properties across samples.

To date, the preparation of biaxially-textured epitaxial NFO thin films has involved pulsed laser deposition (PLD), sputtering or chemical vapor deposition (CVD) techniques. Chemical solution deposition (CSD) has mostly led to NFO and other spinel cubic ferrite thin films with only random grain orientation. An alternative approach, a spin spray method, has been used to deposit ferrite films, but this approach has shown poor stoichiometry control and the resulting films were poorly textured. In the previous chapter, the growth of uniaxially textured polycrystalline NFO films on Si/SiO$_2$/TiO$_x$/Pt(111) (Pt-NFO) substrates is reported. Although (111) orientation normal to the film plane was observed, the films did not show any in-plane orientation.

In this chapter, the fabrication of biaxially textured NFO (111) thin films on c-plane sapphire substrates via CSD is discussed. The NFO films show a strong degree of preferential growth in the <111> direction normal to the film plane and <110> in-plane. The processing conditions are optimized to achieve epitaxial films.
7.2 Approach

To grow the NFO thin films, a 0.5 M NFO solution\textsuperscript{23,24} is spun (8000 rpm × 30 sec) onto pre-cleaned substrates. The films are pyrolyzed at 400 °C for 1 minute and crystallized at 750 °C for 10 minutes in air\textsuperscript{23,24}, resulting in 60 nm-thick NFO films. To vary the film thickness, two set of samples are prepared using 0.2 M and 0.5 M solutions. To study the effect of pyrolysis temperature on crystallinity and texture, the deposited films are pyrolyzed at temperatures ranging from 100 °C to 500 °C for 1 min. The effect of annealing temperature on the film’s texture is also studied for temperatures ranging from 700 to 1000 °C in 100 °C increments. Randomly oriented NFO thin films are grown onto Si/SiO\textsubscript{2} substrates using similar processing conditions for comparison. The film thickness is increased by decreasing the spinning speed.

Standard X-ray diffraction (XRD) θ-2θ scans are performed at room temperature. The in-plane orientation of the NFO film is evaluated by pole figure XRD for \( \chi \) from 0 to 89° on the NFO (222) and (440) planes at \( 2\theta= 37.3^\circ \) and 63.2°, respectively. Epitaxy is explored by XRD φ-scanning of the substrate (01\overline{1}2) plane (\( 2\theta=25.58^\circ, \ \chi=57.76^\circ \)) and the NFO (440) plane (\( 2\theta=63.2^\circ, \ \chi=35.26^\circ \)). Cross-section and top-surface film microstructures are also examined in a helium ion microscope (HIM) and a transmission electron microscope (TEM).

To measure the room temperature magnetization, the magnetic field is applied normal (out-of-plane) and parallel (in-plane) to the film plane. Magnetization data are normalized to the NFO film volume. For the out-of-plane magnetization, a demagnetization factor of 4\( \pi \) is used to correct the effect of the film shape anisotropy\textsuperscript{5}. 

7.3 Results and Discussion

7.3.1 Characterization

Figure 7-1 depicts the XRD pattern of NFO thin films (60 nm) grown onto the c-plane sapphire substrates (Al₂O₃-NFO), indicating the inverse spinel cubic structure of the NFO without any detectable intermediate or secondary phase. For comparison, the XRD pattern of the NFO films of the same thickness, grown onto Si substrates (Si-NFO), is illustrated. While the Si-NFO films show random crystallographic orientation¹³,¹⁴, the Al₂O₃-NFO films reveal a high degree of out-of-plane preferential growth in the <111> direction with a Lotgering orientation factor²⁵ of ~93%. Compared to the complete out-of-plane texture observed in the Pt-NFO films of same thickness in the previous chapter²⁴, however, the degree of texture in the Al₂O₃-NFO films is slightly lower.
Figure 7-1 X-ray diffraction patterns of the biaxially <111> textured and randomly oriented 60 nm-thick NFO films deposited on the c-plane sapphire (Al$_2$O$_3$-NFO) and silicon (Si-NFO).

Figure 7-2 shows the X-ray pole-figure analysis of the Al$_2$O$_3$-NFO films around the NFO <222> and <440> crystallographic directions to evaluate any in-plane orientation in the film. The <222> diffraction intensity concentrated at the center of the pole figure confirms that the NFO grains are mostly aligned along their magnetic easy axis direction, <111>, normal to the film plane.
Figure 7-2 X-ray pole figures associated with (a) <222> and (b) <440> diffractions of the biaxially textured Al$_2$O$_3$-NFO films.

The diffractions, found at a 35.26° inclination in $\chi$ in the <440> pole figure, confirm the preferred orientation of the (111) planes normal to the film plane, but also show that the film has in-plane orientation with 6-fold symmetry along the <111> axis. This is also confirmed by X-ray $\varphi$-scanning of the <0112> Al$_2$O$_3$ and <440> NFO (Figure 7-3).
Figure 7-3 X-ray φ-scans of the <01\overline{1}2> Al₂O₃ substrate and the <440> NFO film.

In the biaxially textured Al₂O₃-NFO films, the average full width at half maximum (FWHM) of 1.5° for the (111) NFO diffraction peaks, as compared to 0.5° for the sapphire (0001), indicates that the film has relatively good epitaxial match to the substrates. Three (01\overline{1}2) sapphire diffraction peaks with 120° intervals originate from the sapphire R\overline{3}c space group with three-fold symmetry along the sapphire [0001] axis (Figure 7-4a). Six discrete peaks in the X-ray φ-scans of the NFO thin films (Figure 7-3), with similar intensity around the [111] crystallographic direction, indicate the presence of a six-fold symmetry in the NFO films. The atomic arrangement of the NFO (111) plane (Figure 7-4b), however, shows a 3-fold symmetry along <111> direction.
The observation of 6-fold symmetry in NFO (111) in the pole figure and $\phi$-scan suggests the presence of $60^\circ$ or $180^\circ$ variants in the in-plane alignment. The dominant in-plane epitaxial relationship between NFO and the substrate is created by matching the (111) NFO planes in two variants rotated by $30^\circ$ with respect to the hexagonal lattice of sapphire (0001), as illustrated in the Figure 7-5. Therefore, two variant epitactic relationships between the NFO film and the c-plane sapphire substrate are:
• [110] NFO ǁ [10\bar{1}0] Al₂O₃
• [110] NFO ǁ [1\bar{1}00] Al₂O₃


Figure 7-5 Schematic diagram of the superposition of NFO (111) and Al₂O₃ (0001) planes in two variants with 30° rotations with respect to the Al₂O₃ structure.

NFO has a cubic spinel structure, while sapphire is a hexagonal corundum (a=0.476 nm, c=1.299 nm) with the Al³⁺ cations located in the distorted oxygen octahedral sites (Figure 7-4a). This epitaxial relationship between a cubic structure and a hexagonally structured substrate is similar
to what is reported for MgAl$_2$O$_4$ and MgFe$_2$O$_4$ spinel thin films on c-plane sapphire substrates
26,27.

The atomic arrangement of the oxygen sublattice in the (111) NFO plane (Figure 7-4b) has the same symmetry as in the (0001)Al$_2$O$_3$, but with a different oxygen-oxygen (O-O) distance. The O-O distance in the (0001)Al$_2$O$_3$ plane is 0.288 nm whereas in the (111)NFO it is 0.294 nm. Thus the oxygen-sublattices’ mismatch is 2.1%. This orientational relationship preserves the close-packing of oxygen planes across the film-substrate interface.

Epitaxial nucleation is enhanced by the low interfacial energy of the NFO (111) planes 28 which, according to the periodic bond chain (PBC) model, have the lowest energy and consequently correspond to the preferential crystal growth planes 28.

7.3.2 Effect of the Film Thickness

The effect of the NFO film thickness on the texture, for thicknesses ranging from 60 nm to 115 nm, is shown in Figure 7-6. In all films, preferred growth in the $<111>$ direction is observed and the highest degree of texture is achieved in the thinnest film (60 nm). This is explained by nucleation/precoalescence texture development governed by the small lattice matching between the (111) NFO and the (0001) sapphire structures. The oriented layers are formed through a heterogeneous nucleation of the aligned nuclei which have epitactic relationships with the sapphire crystal structure (interface nucleation). The nucleation-controlled texture in the Al$_2$O$_3$-NFO films is similar to what is observed in the previous chapter on the NFO films deposited onto the Si/SiO$_2$/TiO$_x$/(111)Pt substrates (Pt-NFO) 29. Analogous to the Pt-NFO films, close
lattice matching (2.1%) accompanied with minimum surface energy of the (111) planes, develops the (111) texture in the Al$_2$O$_3$-NFO films.

The increasing degree of the (111) texture and decreasing intensity of the other peaks is related to randomly orientated grains in the low thickness films can be explained by Schwartz et al. model$^{19}$. In thicker films, the required time for growth of the interface-nucleated grains to reach the surface is higher than in thinner films. Hence, because a higher temperature is reached prior to the completion of the crystallization of initially nucleated grains at the interface, other nucleation events such as surface nucleation and bulk nucleation are possible, which decrease the total degree of texture of the film$^{19}$.

Figure 7-6 X-ray diffraction patterns of the (111) textured NFO thin films on the (0001) sapphire substrates as a function of the NFO film thickness.
Microstructural Studies

Figure 7-7 shows top-view and cross-sectional HIM images of the Al₂O₃-NFO thin films with thicknesses ranging from 60 nm to 110 nm.
Figure 7-7 Helium ion microscopy images of the cross-sections and top views of the Al₂O₃-NFO thin films with thicknesses of (a, e) 110 nm, (b, f) 90 nm, (c, g) 70 nm and (d, h) 60 nm.
A TEM cross-sectional image of the 60 nm-thick film is also shown in Figure 7-8.

![Figure 7-8 TEM cross-sectional image of the 60 nm Al₂O₃-NFO film. The arrows show the interface nucleation of the aligned grains with epitactic relationships with the substrate.](image)

The microscopic images show the interface-nucleated grains and confirm that the observed textured in the NFO films is nucleation-controlled. This is understood by nucleation/precoalescence texture development governed by the small lattice matching between the (111) NFO and the (0001) sapphire structures. The oriented layer is formed through heterogeneous nucleation of the aligned nuclei, which have epitactic relationships with the sapphire crystal structure. The nucleation-controlled texture in the Al₂O₃-NFO films is similar to
what is observed in uniaxially textured Pt-NFO films in the previous chapter. In the Al$_2$O$_3$-NFO films, however, the textured sublayer has in-plane texture as well as the out-of-plane $<111>$ orientation. The interface-nucleated NFO crystallites are strongly influenced by the substrate atomic arrangement and follow the epitaxial relationships. The surface-nucleated NFO grains, however, are randomly oriented, explaining similarity in grain shape and size in the plan view images of Figure 7-7 and the higher degree of $<111>$ orientation achieved with decreasing film thickness (observed in the XRD patterns of the Al$_2$O$_3$-NFO films with thicknesses varying from 60 nm to 110 nm, Figure 7-6). Since in the 110 nm-thick NFO films, the bulk nucleation (homogenous) across the film thickness can be seen in the cross-sectional image (Figure 7-7a), the volume fraction of the randomly oriented grains is higher than that in the thinner films. The HIM images also show increased porosity in the thicker film.

*Magnetic Properties*

The in-plane and out-of-plane magnetization hysteresis loops for the 60 nm-thick, biaxially textured Al$_2$O$_3$-NFO films are shown in Figure 7-9. The out-of-plane texturing of the NFO films along the magnetic easy-axis $<111>$ results in a strong perpendicular magnetic anisotropy. In NFO, the [111] direction is the direction of spontaneous domain magnetization in the demagnetized state. The presence of out-of-plane anisotropy is consistent with the observation of lower saturation magnetic field and the more square shape of the out-of-plane magnetization hysteresis loop relative to the in-plane hysteresis curve. As a result, for the textured NFO thin films, higher $M_r/M_s$ ratio is measured in the out-of-plane magnetization (79%) than in the in-
plane measurement (50%). The out-of-plane $M_r/M_s$ ratio is also higher than that of the randomly oriented Si-NFO thin films (30%) and of the uniaxially textured Pt-NFO thin films (70%).

![Figure 7-9 Room temperature in-plane and out-of-plane magnetization hysteresis for the 60 nm-thick biaxially textured Al$_2$O$_3$-NFO films.](image)

Figure 7-9 Room temperature in-plane and out-of-plane magnetization hysteresis for the 60 nm-thick biaxially textured Al$_2$O$_3$-NFO films.

The out-of-plane magnetic response exhibits larger hysteresis with coercivity ($H_c$) close to ~310 Oe (24.7 kA/m) compared to the in-plane $H_c$ ~ 160 Oe (12.7 kA/m) (Figure 7-9 inset). Due to the shape anisotropy in thin films, the coercivity is amplified in the out-of-plane measurement. The shape anisotropy in thin films favors the in-plane magnetic moment orientation in order to...
minimize the magnetostatic energy $^3$. For the biaxially textured Al$_2$O$_3$-NFO thin films, however, the coercivity enhancement (106%) is smaller than that in the randomly oriented Si-NFO thin films (290%) and in the uniaxially textured Pt-NFO thin films (125%) of the same thickness $^{24}$. The effect of the film thickness on the out-of-plane coercivity for the biaxially textured Al$_2$O$_3$-NFO films is shown in Figure 7-10a. The coercivity increases from 300 Oe (23.9 kA/m) for the 60 nm-thick to 380 Oe (30.2 kA/m) for the 110 nm-thick films. For the 110 nm-thick film, this value is almost half of the coercivity for the non-textured Si-NFO films and is 20% lower than that in the uniaxially textured Pt-NFO film $^{24}$. It has been previously reported that presence of high angle grain boundaries and non-magnetic inclusions (e.g. porosity) can act as impediments to domain wall movement $^{30}$. Hence, the low density of high angle grain boundaries in the epitactic Al$_2$O$_3$-NFO sub-layer (interface-nucleated grains), as well as the more compact grain structure and reduced porosity, are possible reasons for the lower coercivity values in these films relative to the Pt-NFO films.

The magnetization, and specifically the $M_r/M_s$ ratio (which is an index of the magnetic anisotropy), slowly increases with decreasing the film thickness, as shown in Figure 7-10b; a trend similar to what is observed in the Pt-NFO films (previous chapter) $^{24}$ but with higher values in the Al$_2$O$_3$-NFO films. $M_r/M_s$ ratio for 110 nm-thick randomly oriented Si-NFO and the uniaxially textured Pt-NFO films are shown for comparison. The out-of-plane $M_r/M_s$ ratio improves from 50% in the 110 nm-thick film to 79% in the 60 nm-thick Al$_2$O$_3$-NFO films. Similar to the Pt-NFO $^{24}$, the deviation from perfect perpendicular magnetic anisotropy and a square hysteresis loop is due to the randomly-oriented grains atop the epitactic sub-layer (bulk
and surface-nucleated grains), reducing the magnetic anisotropy. Another possible contributing factor is the strain induced into the NFO films due to lattice misfit and the thermal stresses resulting from the thermal expansion mismatch between the film and substrate. Given the low magnetic anisotropy of the NFO \(K_1 \approx -10^4\), lattice strain can dominate the effect of the texture (magnetocrystalline anisotropy), especially at low thickness. With low magnetic anisotropy and the small negative magnetostriction constant of the NFO \(\lambda_s =50\) ppm, the internal stress can dominate the magnetic anisotropy \(^{30}\).
Figure 7-10 Room temperature out-of-plane coercivity and $M_r/M_s$ ratio for the Al$_2$O$_3$-NFO films as a function of film thickness. Values for the 110 nm-thick randomly oriented Si-NFO and the uniaxially textured Pt-NFO films $^{23,24}$ are shown for comparison.

Compared to the uniaxially textured Pt-NFO films $^{24}$, the biaxially textured Al$_2$O$_3$-NFO films show a 10% increase in $M_r/M_s$ ratio and a 20% reduction in the out-of-plane coercivity. These improvements correlate to reduced thermal and misfit strains in the Al$_2$O$_3$-NFO relative to the Pt-NFO due to smaller difference in thermal expansion coefficient and lattice misfit between the Al$_2$O$_3$ and NFO. The Al$_2$O$_3$-NFO films show comparable $M_r/M_s$ ratio to the epitaxial NFO films.
sputtered onto SrTiO$_3$ and Y$_{0.15}$Zr$_{0.85}$O$_2$ single crystal substrates and annealed at 1000 °C (~80%).

Compared to PLD-grown epitaxial NFO films on MgO substrates, the Al$_2$O$_3$-NFO films show lower $M_r/M_s$. The PLD-prepared films were deposited at 900 °C and annealed at 1000 °C for 4 hours, resulting in a 1400 nm-thick epitaxial NFO film on the MgO substrate with nearly perfectly square-shaped out-of-plane magnetization. While the higher thermal budget improves the texture in the NFO film, it increases the potential elemental interdiffusion between the substrate and the film. Therefore, although the Al$_2$O$_3$-NFO biaxially-textured films are deposited and annealed at much lower temperatures than previously reported epitaxial/textured NFO, the magnetic anisotropy achieved is still comparable at the same thicknesses.

7.3.3 Processing Optimization

*Effect of the Pyrolysis Temperature*

Figure 7-11 illustrates the XRD patterns of 100 nm-thick NFO films pyrolyzed at different pyrolysis temperatures from 100 °C to 500 °C for one minute and annealed at 750 °C for 10 min. The patterns show formation of inverse spinel cubic NFO phase with preferential growth in the $<111>$ direction for all pyrolysis temperatures. The samples pyrolyzed at 400 °C and 500 °C, however, show the higher degree of $<111>$ texture.
Figure 7-11 X-ray diffraction patterns of the textured NFO films deposited onto the (0001) sapphire substrates. The films are pyrolyzed at temperatures ranging from 100 °C to 500 °C and annealed at 750 °C for 10 min. The inset shows the changes of (111) Lotgering factor (f) as a function of pyrolysis temperature.

The Lotgering factor (f)\textsuperscript{25} for the <111> orientation is calculated using the following equations:

\[
f = \frac{p - p_0}{1 - p_0}; \quad p = \frac{\sum I_{(hhl)}}{\sum I_{(hkl)}};
\]

where \( p \) is the ratio of the intensity for (hhl) peaks to the total intensity of all peaks and \( p_0 \) is the same ratio for the randomly orientated sample. The “f” changes by changing the pyrolysis temperature and the film pyrolyzed at 400 °C shows the highest degree of <111> texture as 80%, as shown in the Figure 7-11 inset. However, the <111> X-ray diffraction peaks are broad and
shallow, while there is still a small trace of the (311) peak; likely indicating of surface nucleation of randomly oriented grains and small grain size. The difference in degree of orientation of the films pyrolyzed at various temperatures can be explained by the model proposed by Schwartz et al. \(^3\) on the competition between two heterogeneous nucleation events; the interface nucleation of oriented grains and the surface nucleation of randomly oriented grains. According to their model, the nucleation at the surface is less favorable than the nucleation at the interface with proper lattice matching with the substrate, but more favorable than true homogenous nucleation in the bulk. Hence, the final film microstructures are governed by the energy barrier for each nucleation as well as the grain growth kinetics. Therefore, at a same heating rate, given the higher energy barrier for surface nucleation than for interficial nucleation, in the film pyrolyzed at lower temperature, there is less time for growth of the interface-nucleated grains (oriented grains) before the onset of surface nucleation of the randomly oriented grains. In contrast, in the film pyrolyzed at higher temperature, due to larger differences between energy barriers, the time is sufficient to allow the oriented grains to grow and consume the amorphous phase prior to onset of surface nucleation \(^3\).

Figure 7-12 compares the top view HIM images of the samples pyrolyzed at 100 °C and 500 °C at two magnifications. Both top view structures show similar grain shape and size of about 40 nm in diameter on average indicating formation of the surface-nucleated grains. The microstructure of the film pyrolyzed at lower temperature, however, shows increased porosity, which is correlated to continuous solvent release during annealing, while in the other film, all the solvent may be released before the onset of nucleation and growth.
Figure 7-12 Top-view HIM micrographs of single-layer NFO films on (0001) sapphire substrates, pyrolyzed at (a,b) 100 °C and (c,d) 500 °C for one minutes.
The analogous microstructure between the films pyrolyzed at different temperatures is also consistent with what is observed in the randomly oriented NFO thin films on Si substrates (chapter 4, figure 4-3).

*Effect of Annealing Temperature*

The effect of the annealing temperature on the <111> texture in 100nm-thick NFO films for temperatures ranging from 700 °C to 1000 °C and fixed annealing time (10 min) is shown in Figure 7-13. Before annealing, all samples are pyrolyzed at 400 °C for 1 min; the pyrolysis temperature in which the films show the highest degree of orientation. Increasing the annealing temperature from 700 to 1000 °C results in growth of the peaks corresponding to the randomly orientated grains, while the intensity of the <111> family peaks remain unchanged.
Figure 7-13 X-ray diffraction patterns of the textured NFO films deposited on the (0001) sapphire substrates, pyrolyzed at 400 °C for 1 min and annealed at temperatures ranging from 700°C to 1000 °C for 10 min.

The highest “f”, achieved for the annealing temperature of 750 °C, is 80%. The decreased texture in the films annealed at higher temperatures is explained by the higher energy barrier for the surface nucleation of randomly orientated grains which can be surmount by higher energy input at the higher annealing temperatures. The surface-nucleated grains also grow more due to the higher diffusion rate at higher temperature leading to larger grain size (70 nm) and higher surface roughness (rms value of 6.3±0.3 nm), as shown in Figure 7-14. In contrast, for lower annealing...
temperature (e.g. 750 °C), the surface-nucleated grains are observed but the grain size (40 nm) and hence surface roughness (rms value of 3.8±0.4 nm) is much lower.

Figure 7-14 Top-view HIM micrographs and corresponding AFM images of single-layer NFO films on (0001) sapphire substrates and annealed at (a,c) 750 °C and (b,d) 1000 °C for 10 minutes.
Effect of the Solution Concentration

Regarding to our previous results on effect of the film thickness on the degree of NFO texture\textsuperscript{29}, in which the thinner films resulted in the higher degree of texture, two different solution molarities (0.2 M and 0.5 M) are used to grow NFO thin films with different thicknesses. Figure 7-15 shows the XRD pattern for the Al\textsubscript{2}O\textsubscript{3}-NFO films deposited using 0.2M and 0.5M solutions and processed at the same conditions. The lower molarity solution results in fully $<111>$ oriented 40 nm-thick NFO films on sapphire. The film thickness affects the film microstructure owing to the time required for growing interface-nucleated (oriented) grains through consumption of the amorphous materials, and the need to reach to the surface prior to onset of surface nucleation. The required time for the complete growth of these grains is less in the thinner films than in the thicker films. Hence, surface nucleation is less probable in the thinner films.

In the epitaxial NFO films, the in-plane epitaxial relationship between the films and the substrates is evaluated by X-ray $\phi$-scanning of (01-12) Al\textsubscript{2}O\textsubscript{3} and (440) NFO, as shown in the Figure 7-15 inset. As observed in pole figure analysis (Figure 7-2), the NFO films show the sixfold symmetry along the $<111>$ axis with 30° rotation with respect to the sapphire peaks. The average full width at half maximum (FWHM) value of NFO peaks is estimated by 1.5°, which show relatively good epitaxial matching between the NFO(111) and the sapphire (0001)\textsuperscript{29}.
Figure 7-15 X-ray diffraction patterns of textured NFO films deposited onto the (0001) sapphire substrate, using 0.2 M and 0.5 M solutions. The inset shows the X-ray φ-scan of the (01-12) $\text{Al}_2\text{O}_3$ and (440) NFO in the epitaxial films deposited using 0.2M solution.

Figure 7-16 depicts the top view HIM image of the epitaxial (111) NFO thin film. As discussed previously, the (111) NFO and (0001) sapphire are epitaxially related in two in-plane variants of [110] NFO $\parallel$ [1010] $\text{Al}_2\text{O}_3$ or [2100] $\text{Al}_2\text{O}_3$, which are rotated by 60 degree with respect to each other, as shown in the Figure 7-16. Nucleation of small grains, mostly at the kinks, indicates the surface diffusion of atoms to kink sites, which are energetically more favorable for nucleation. In this sample, due to low film thickness, most of the interface-nucleated, oriented grains have completely grown and reached the surface prior to the onset of the surface nucleation.
Figure 7-16 (a,b) Top-view HIM micrographs of the epitaxial (111) NFO thin films deposited onto the (0001) sapphire substrates. (c) schematic of two rotated (111) NFO planes in two variants with 60 or 180 degree rotation.

Epitaxial growth and the suggested relationship, are confirmed using selected area electron diffraction (SAED) pattern illustrated in Figure 7-18. The diffraction pattern is taken from
(0001)Al₂O₃/(111)NFO zone axis. Two rotated sets of NFO spots with three-fold symmetry are clear in the pattern.

Figure 7-17 (a) Selected area electron diffraction (SAED) pattern of the (111)NFO and (0001)sapphire and (b) its indexed pattern.

7.4 Summary
Biaxially textured (111) NiFe₂O₄ thin films are grown onto c-plane sapphire substrates using chemical solution deposition. In addition to the strong (111) out-of-plane texture, the TEM and HIM microstructural studies show that the lattice structure of the films are oriented in two
variants with respect to the substrate plane. Both variants are rotated by 30 degree relative to the substrate (0001) plane.

Similar to the Pt-NFO films in chapter 6, decreased NFO film thickness results in a higher degree of (111) texture. The magnetic properties of the biaxially textured films improve in remanent magnetization compared to the randomly oriented Si-NFO and uniaxially textured Pt-NFO thin films. However, even in the thinner film with highest degree of out-of-plane texture, the magnetic properties show a slight deviation from the perfect square shape hysteresis. This can be explained mainly by the strain in the film due to lattice misfit and the thermal expansion coefficient mismatch between the film and the substrate.

The film processing conditions including pyrolysis temperature, annealing temperature and time are optimized to obtain epitaxial NFO films. It is shown that pyrolysis temperature at 400 °C and annealing at 750 °C results in the highest degree of <111> texture in NFO thin films.

7.5 References:


30 G. F. Dionne, Magnetic Oxides (Springer Science and Business Media, LLC, Boston, MA, 2009).
8.1 Conclusions

This dissertation presents a systematic investigation on the texturing of the NiFe$_2$O$_4$ (NFO) thin films in its easy axis direction to improve the magnetostrictive properties for applications in multilayer magnetoelectric composites. In the chapter 4, a new chemical solution procedure was developed to produce phase-pure NFO thin films. The solution and the films were characterized and effect of the processing conditions including pyrolysis temperature and annealing temperature and time were studied on the microstructure and magnetic properties of the nanocrystalline NFO thin films on Si substrates. In chapter 5, NiFe$_2$O$_4$/Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ (NFO/PZT) thin film multilayer magnetoelectric composites were prepared on Si substrates in two configurations to investigate the compatibility of the coupled phases for application in magnetoelectric laminated composites. The microstructure of the multilayers was studied and the magnetic and electrical properties of the NFO and PZT were investigated in the multilayers. To improve the magnetic properties of the magnetic phase (NFO) the NFO was grown and studied on platinized Si (Si/SiO$_2$/TiO$_x$/Pt) (chapter 6) and (0001) sapphire substrates (chapter 7).

The main findings of this dissertation can be summarized in following points:

✓ A new 2-MOE (CH$_3$OCH$_2$CH$_2$OH) solvent-based chemical route was developed to deposit NiFe$_2$O$_4$ (NFO) thin films.
Randomly-oriented, phase-pure NFO thin films with inverse spinel structure and granular morphology with grain size of 40 nm were grown onto Si (100) substrates using the proposed chemical solution process.

Changes in the pyrolysis temperature did not affect the film morphology and the magnetic properties.

Increased annealing temperature results in enhanced saturation magnetizations.

The TEM microstructural studies exhibited that neither any interdiffusion between the film and substrate nor any impurity or secondary phases was observed in the film annealed at different annealing temperatures.

Two magnetoelectric multilayer geometries were fabricated from spinel cubic NFO and tetragonal perovskite PZT phases (Si/NFO/PZT and Si/NFO/Pt/PZT) via chemical solution processing.

No detectable secondary/impurity phase was detected in two phases.

The TEM microstructural studies revealed a sharp interface between the NFO and PZT layer, which is necessary in magnetoelectric laminated composites.

It was shown that the presence of an intermediate Pt layer was necessary to reduce elemental diffusion (e.g Pb, Zr) from the PZT into the NFO and the substrate. Pt was also required as a bottom electrode to collect the electrical charge out of the PZT layer.
• The saturation polarization ($P_s$) and coercive electric field ($E_c$) of the Si/NFO/Pt/PZT multilayer were comparable to those reported for sol-gel derived PZT films of similar composition and thickness.

• The magnetic properties of the NFO layer in the multilayers showed improvement in saturation magnetization and decrease in coercivity compared to the Si/NFO thin films of the same thickness.

✓ To improve the magnetic properties of the NFO layer for many applications including magnetoelectric composites, highly textured (111) NFO thin films were prepared on Si/SiO$_2$/TiO$_x$/Pt (111) substrates using the proposed chemical solution processing.

  • With a high degree of out-of-plane texture in the $<111>$ direction, the Pt/NFO films did not show any in-plane orientation.

  • With decreasing the NFO films’ thickness, nearly complete uniaxial texture is achieved.

  • The TEM microstructural studies show that the textured growth is nucleated by lattice matching at the Pt/NFO interface which is also enhanced by the low surface energy of the (111) NFO planes.

  • The magnetic properties of the textured films show improvements in remanent magnetization and coercivity relative to the randomly oriented films and are comparable to those grown by PLD and sputtering of the same thickness.
Biaxially textured NiFe₂O₄ thin films were prepared on c-plane Al₂O₃ substrates.

- In addition to a strong degree of out-of-plane texture in the <111> direction, the NFO films on sapphire show in-plane orientation in two variant with respect to the substrate. The (111) NFO and (0001) sapphire are epitaxially related in two in-plane variants of [110] NFO || [10\bar{1}0] Al₂O₃ or [1\bar{1}00] Al₂O₃, which are rotated by 60 degree with respect to each other.

- Similar to the NFO films on Si/SiO₂/TiOₓ/Pt substrates, decreased NFO film thickness results in a higher degree of (111) texture.

- The magnetic properties of the biaxially textured films improve in remanent magnetization compared to the randomly oriented Si-NFO and uniaxially textured Pt-NFO thin films.

- The coercivity of the biaxially textured NFO thin films is lower than the uniaxially textured.

- The magnetic properties of the uniaxially textured NFO films are comparable to the films of same thickness grown by PLD and sputtering techniques.

- The film processing conditions including pyrolysis temperature, annealing temperature and time are optimized to obtain epitaxial NFO films. It is shown that pyrolysis temperature at 400 °C and annealing at 750 °C results in the highest degree of <111> texture in NFO thin films.
8.2 Recommendation for Future Work

- Textured NiFe$_2$O$_4$ can be a good candidate to be coupled with the piezoelectric phases including Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ in magnetoelectric composites. As it is shown the biaxially textured NFO exhibits higher magnetic and magnetostrictive response than uniaxially textured and randomly oriented films. Hence, it would be interesting to address this question if a high magnetoelectric coupling will be achieved in the composites prepared by textured NFO as the magnetic phase.

- Other ME laminated composite configurations of textured NFO and PZT as the piezoelectric phase can be prepared since it is shown that growth of PZT on platinized Si substrates results in highly (001) textured PZT with large piezoelectricity. To achieve the maximum ME coupling response it will be required to optimize the relative thickness of the magnetic and piezoelectric phases in different configurations of laminated ME composites.

- For many applications including memory devices it is required to have films with perfect out-of-plane anisotropy (100% remanence ratio). Regarding small magnetocrystalline anisotropy constant of NFO, to have a perfect anisotropy it is necessary to have higher film thickness to overcome the strain effect in the film. Hence, that would be very useful to address this question how to increase the textured NFO film without changing the degree of texture.

- Adding Zn to nickel ferrite makes them intended for very high frequency operation (more than 100 MHz) because of their high initial permeability and low coercivity. Having
these Zn-nickel ferrite compounds textured makes them even more suitable for high frequency application because of their low magnetic loss.

- Besides maximizing the magnetostrictive response of the magnetic phase in the magnetoelectric composite, to improve the ME response, it is required to tailor the piezoelectricity of the piezoelectric phase by texturing it.

- Lastly, the proposed chemical route has this potential to be adjusted and modified to obtain other magnetic ferrites such as cobalt ferrite. Cobalt ferrite has much higher magnetostrictive response at room temperature than nickel ferrite. Therefore, it is expected using the proposed chemical solution, textured cobalt ferrite thin films can be prepared for applications in ME composites.

8.3 References